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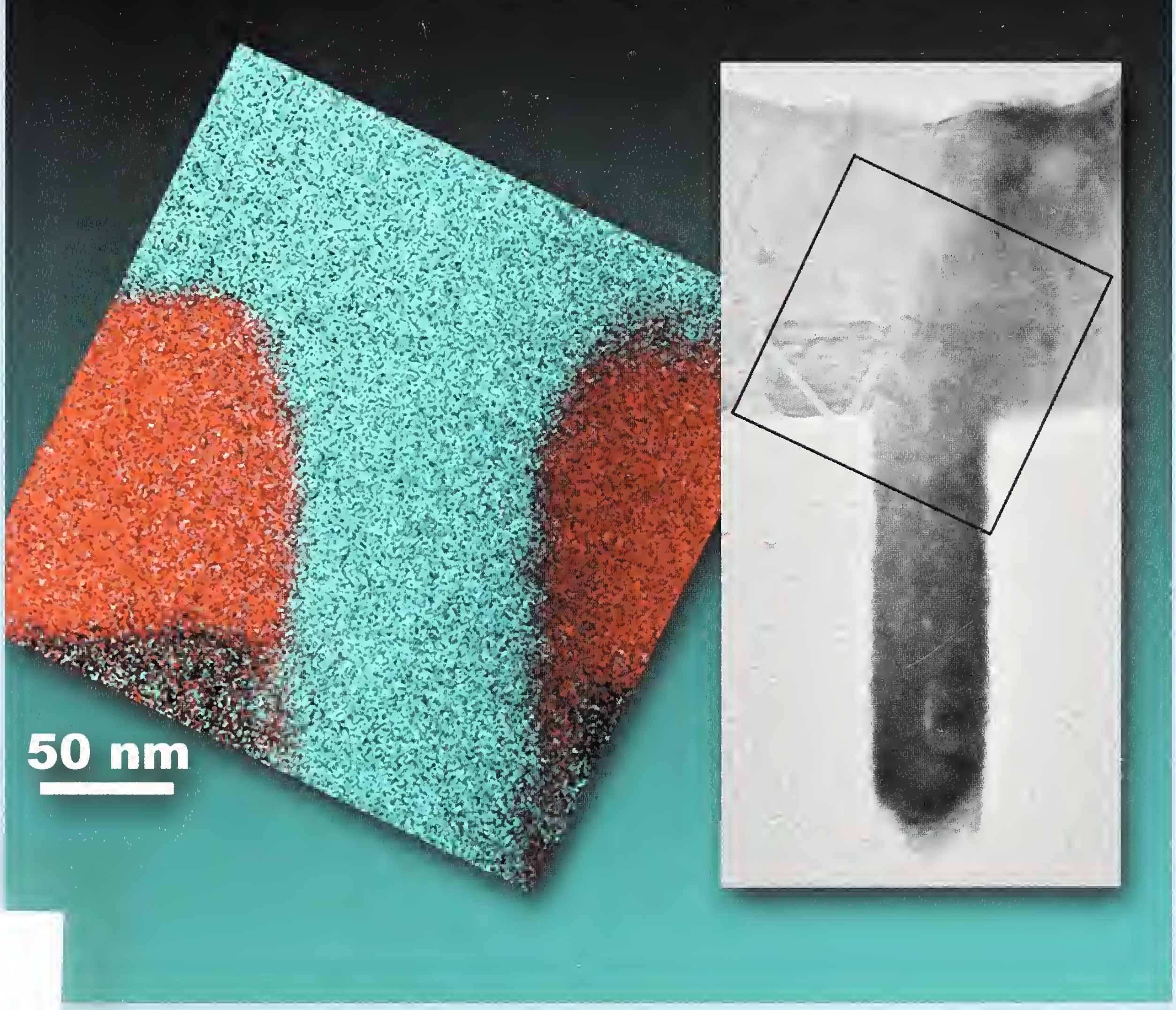
September 2001

# MSEL

## FY 2001 PROGRAMS AND ACCOMPLISHMENTS

# METALLURGY DIVISION

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**On the Cover:**

Cross-section of a nanoscale trench (dimensions of 90 nm wide and 500 nm high), fabricated with an initial seed layer of copper, later filled with electrodeposited nickel. Transmission electron microscopy and compositional mapping reveal salient features on the nanometer scale: electron energy loss spectroscopy was used to generate a compositional map (left), where the red color indicates copper and blue denotes the nickel region. The cross-sectional TEM image (right) reveals microstructural features (note the planar twins in the copper seed layer). Such information supports the development of new electrodeposition metrology techniques for micro- and nano-electromechanical devices (MEMS/NEMS).

**National Institute of Standards and Technology**
Karen H. Brown,
Acting Director

**Technology Administration**

**U.S. Department of Commerce**
Donald L. Evans,
Secretary

DEPARTMENT OF COMMERCE
UNITED STATES OF AMERICA

# MATERIALS SCIENCE AND ENGINEERING LABORATORY

## FY 2001 PROGRAMS AND ACCOMPLISHMENTS

## METALLURGY DIVISION

Carol A. Handwerker, Chief

Frank W. Gayle, Deputy

Richard E. Ricker

NISTIR 6797

September 2001

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# Executive Summary

The mission of the NIST Metallurgy Division is to provide critical leadership in the development of measurement methods, standards, and fundamental understanding of materials behavior needed by U.S. materials producers and users to become or remain competitive in the changing global marketplace. As a fundamental part of this mission we are responsible not only for developing new measurement methods with broad applicability across materials classes and industries, but also for working with individual industry groups to develop and integrate measurements, standards, software tools, and evaluated data for specific, technologically important applications.

With our mission in mind we establish our research priorities through extensive consultation and collaboration with our customers in U.S. industry and with our counterparts in the international metrology community, using the following criteria:

• Magnitude and immediacy of industrial need

• Match to our mission

• Whether the NIST contribution is critical for success

• Anticipated impact relative to our investment

• Our ability to respond in a timely fashion with high-quality output

• Opportunity to advance mission science

Using these criteria, our priorities are established by the Division's technical leaders through formal and informal means, including industrial roadmapping activities, workshops, technical meetings, standards committee participation, and individual consultation with our customers. Within the context of industrial relevance and potential impact of our research, technology trends strongly influence the technical directions addressed in Metallurgy Division programs. We prefer to work in rapidly evolving technologies, where advances in measurement science are needed to understand the limitations on system behavior, and, thereby, address issues where our contributions are likely to have an impact on the course of technology.

The Division is composed of 39 scientists, supported by 6 technicians, 6 administrative staff members, and more than 30 guest scientists, organized into five groups that represent the Division's core expertise in Metallurgical Processing, Electrochemical Processing, Magnetic Materials, Materials Structure and Characterization, and Materials Performance. However, by virtue of the interdisciplinary nature of materials problems in the industrial and metrology sectors that we serve, Program teams are assembled across group, division and laboratory boundaries to best meet our project goals. We are committed to assembling the expertise and resources to fulfill our technical goals with the speed and quality necessary to have the desired impact.

Our current research portfolio focuses on fulfilling specific measurement needs of the magnetic data storage, microelectronics packaging, automotive, aerospace, and optoelectronics industries and on establishing national traceable hardness standards needed for international trade. Our output consists of a variety of forms, from scientific publications elucidating fundamental materials behavior to measurement techniques, standard reference materials, evaluated data, software tools, and sensors for on-line process control.

**Magnetic Data Storage:** In the program on Materials for Magnetic Data Storage, we are examining issues of magnetization control in thin films through the development of microstructure-processing-property relationships for giant magnetoresistance (GMR) spin valves, ferromagnetic measurements and modeling for magnetization control in thin films, a suite of SRMs for magnetic calibration, an international working group creating standard problems to test micromagnetics software used to design magnetic structures, and measurements of magnetic properties of dispersed nanomaterials. In the past year we have started two new major projects in this program. As part of the National Nanotechnology Initiative, a major collaboration between MSEL and the Electronics and Electrical Engineering Laboratory (EEEL) is developing new measurement methods and models for magnetic damping, needed by the magnetic data storage industry in the next 3-5 years to increase switching speed. Our long-term project on GMR thin films is being refocused into Spintronics, the use of spin-polarized electrons for new devices and magnetic imaging. Through an extensive network of university and industrial collaborators, we are using the process measurement and control capabilities of the MSEL Magnetic Engineering Research Facility to develop an understanding of the materials structure and processing issues in the creation and transfer of spin-polarized electrons.

**Microelectronics Packaging:** In the MSEL Program on Materials for Microelectronics, we are providing tools for producing improved metal interconnects, from copper on-chip interconnects at the nanometer scale to wire bonding to solder joints on printed wiring boards. Our project on measurements and modeling of electrodeposited copper for nanometer scale chip interconnection technology has produced significant value to the microelectronics community. In the two years since beginning the project, we have developed a measurement technique, a theory for control of interface dynamics, and modeling software for predicting quantitatively the ability of complex electrolytes to fill vias and trenches, and have transferred all of these to the appropriate industrial customers. During the last six months we have demonstrated the generality of the theory to electrodeposited metals other than copper, and are examining its relevance to nanoelectromechanical systems (NEMS). Our expertise in soldering alloys and processes has led us to work with U.S. industry to develop alternative technologies mandated by international environmental legislation: US manufacturers feel an urgency to have the ability to assembly circuit boards with lead-free solders due to impending restrictions in Japan and Europe. We have been working with an NCMS Consortium since 1997 and with a NEMI Task Force since 1999 to evaluate the manufacturing and reliability of lead-free solders.

**Automotive:** Within the expanding program on the Forming of Lightweight Materials, we are developing standard test methods for sheet metal forming, measurements of surface roughness, and physically based constitutive laws and measurement tools

needed to reveal them. This year we completed the development of process models and data to improve the manufacturing of metal matrix composites for drivetrain components and will continue to work with our industrial partners to apply these models to production. Our new projects are also done in close collaboration with the automotive industry through formal partnerships, such as the United States Council for Automotive Research (USCAR) and the Partnership for a New Generation of Vehicles (PNGV), and will help accelerate the design of forming operations for lightweight materials such as aluminum, that will ultimately improve fuel economy.

**Aerospace and Power Generation:** Within the Metals Processing Program, we continue to help U.S. aerospace and power generation industries improve responsiveness and competitiveness by accelerating the design of manufacturing processes for turbine engines. In the past year we have completed the thermodynamic database for use by casting foundries in commercial software for modeling solidification of eleven component systems. Our reaction path analysis of multicomponent alloys, also developed this year, is being evaluated by our industrial partners for use in alloy and process design.

**Optoelectronics:** As a result of a growing collaboration between EEEL and MSEL, a Program on Wide-Band Gap Semiconductors was established at the end of FY2001. Building on the existing projects on metal interconnects for GaN (Metallurgy Division) and on interface and bulk defects in GaN (Ceramics Division), the EEEL-MSEL program will develop a comprehensive suite of measurement methods for characterizing interface and bulk defects limiting the application of GaN and related materials.

**National Hardness Standards:** In addition to industry-specific goals, national and international standardization activities are a continuing responsibility. As part of our core NIST mission, we provide national and international leadership in the standardization of Rockwell hardness, the primary test measurement used to determine and specify the mechanical properties of metal products. Our responsibility requires us not only to develop the US national standards with traceability from NIST through NVLAP to secondary standards labs and US metals producers and users, but also to provide leadership to ASTM Standards Committees, the US delegation to ISO, BIPM, and OIML.

In addition to starting or expanding program areas in FY2001, we have completed projects in Thermal Spray Processing, High-Temperature Fatigue Resistant Solders, Magnetization Control in Thin Films, and Mechanical Properties of Multilayered and Nanomaterials. In FY2002 the staff members and resources from these projects ($\approx 18\%$ of the Division financial resources) will shift to the areas described above. One possible new program for FY2002 is being evaluated in response to 2001 industrial roadmapping and consortium building for powder processing, particularly for automotive applications.

In addition to these programs there are three themes that cut across these topical areas. Combinatorial/high-throughput methods, computational materials science, and internet delivery of NIST output will have a profound effect on the way we do business in the next five years. Combinatorial methods are designed to rapidly generate knowledge of materials properties by the fabrication and measurement of extensive arrays of extremely small sample elements, followed by data collection and analysis. In the corporate R&D environment, the aim of combinatorial research is the identification of new materials with product-specific characteristics. Combinatorial methods are in their infancy. Through the development of the NIST Combinatorial Methods Research Center, NIST has the opportunity to contribute to the measurement infrastructure needed to exploit this concept. Likewise, computational materials science will help reveal increasingly complex relationships among materials composition, nano and microstructure, and properties. The MSEL Center for Theoretical and Computational Materials Science plays a leading role in the development of software tools needed in our programs and is directed by Metallurgy Division staff. Software tools will continue to be a major part of our strategy for delivering materials models, and the internet will be the most important mechanism for transferring not only software, but also, data, measurement methods, and fundamental information on materials behavior.

In FY2001, Metallurgy Division staff members were recognized for their outstanding contributions to measurement science and technology transfer in the areas of solidification and magnetism. For his pioneering work in crystal growth and solidification, Sam Coriell was made a Fellow of the American Physical Society in March 2001 and was awarded the triennial F. C. Frank Award (co-shared with Don Hurle) by the International Organization for Crystal Growth in Kyoto, Japan (July, 2001). William Boettinger received the 2001 TMS Bruce Chalmers Award, in New Orleans (February 2001), "for showing how fundamental thermodynamic and kinetic models, with modern computational power, lead directly to quantitative predictions of the microstructure generated by solidification." Dr. Boettinger was also named the Van Horn Lecturer at Case Western Reserve University, April 2001 and the Robert B. Pond, Sr. Distinguished Lecturer at The Johns Hopkins University, May 2001. Robert McMichael was awarded the NIST Samuel Wesley Stratton Award for his internationally acclaimed research on measurements and modeling needed for magnetization control in thin film; this is NIST's highest award for scientific excellence.

In this report we have tried to provide insight into how our research programs meet the needs of our customers, how the capabilities of the Metallurgy Division are being used to solve problems important to the national economy and the materials metrology infrastructure, and how we interact with our customers to establish new priorities and programs. We welcome feedback and suggestions from our customers on how we can better serve their needs and encourage increasing collaboration with them to this end.

Carol A. Handwerker
Chief, Metallurgy Division

# Technical Highlights

The following Technical Highlights section includes expanded descriptions of research projects that have broad applicability and impact. These projects generally continue for several years. The results are the product of the efforts of several individuals. The Technical Highlights include:

- Electrodeposited Copper for On-chip Interconnects: Tools for the Microelectronics Industry
- High Temperature Lead Free Solders: Tools for the Microelectronics Industry
- Process Modeling of Low Cost Powder Metallurgy Technology for Particle Reinforced Aluminum
- Standard Problems for Computational Micromagnetics
- Particle Temperature Measurement Issues for Thermal Spray Processing
- NIST Research for Springback Predictability and Sheet Metal Forming in the Auto Industry
- Thermodynamic and Kinetic Modeling of Multicomponent Alloys

# Electrodeposited Copper for On-Chip Interconnects: Tools for the Microelectronics Industry

*The introduction of copper metallization and low dielectric constant materials into chip manufacture is the most difficult interconnect challenge of modern microelectronics. Current state-of-the-art chips have interconnects, or on-chip "wiring," as narrow as 150 nm to 180 nm with height to width ratios as great as 2:1. The filling of such trenches with copper can currently be accomplished by electrodeposition, but roadmaps for the semiconductor industry state needs for trenches as narrow as 50 nm with a 10:1 aspect ratio. Researchers at NIST are providing the fundamental understanding required to achieve these goals. Models of the mechanism behind superfilling during copper electrodeposition, and associated computational and measurement tools developed at NIST are addressing the needs of the microelectronics community and are already in use by industry to streamline the development of electrodeposition baths.*

The semiconductor industry has recently shifted from the use of aluminum for interconnects, or on-chip "wiring," in integrated circuits to copper because of its lower resistivity and higher electromigration resistance. Electrodeposition has been found to be the best means to deposit copper into the narrow, deep trenches used for circuitry, since "superconformal" deposition is possible which fills very narrow trenches without porosity.

An electrolytic copper linewidth of 180 nm is now commonly found in Integrated Circuit fabrication. Extension to the narrower and deeper lines needed in the next generation of IC requires industrial development of new electrolytes and deposition schemes. Development of plating baths able to deposit in trenches with aspect ratios (height/width) as high as 10:1 is limited by the necessity of time-consuming, resource-intensive evaluations with actual nano-scale patterned substrates. Such experiments require microstructural characterization by focused ion beam (FIB), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) on an individual basis.

NIST efforts address metrology needed for superconformal deposition that minimizes this time-consuming experimental work. The mechanism responsible for superconformal electrodeposition of copper in high aspect ratio features has been determined. Simulations from a model based on this mechanism have been shown to predict results of electrodeposition filling experiments in trenches as small as ≈90 nm wide and ≈450 nm deep. No fitting parameters are required to model this behavior.

This work has built upon two recent Metallurgy Division discoveries. First, an electrolyte was developed that yields superconformal electrodeposition of copper. Second, voltage cycling-induced hysteresis of copper deposition rate on flat copper specimens was shown to be indicative of the ability of an electrolyte to yield superconformal deposition. Superconformal deposition was shown to occur only when both an inhibiting additive and an accelerating additive are present in the electrolyte.

Kinetic parameters for particular electrolytes are obtained from the cyclic voltammetry described above. These kinetic parameters describe the rate at which the accelerating additive accumulates on the copper surface, displacing the inhibiting additive that retards local copper deposition. They also quantify the impact this accumulation has on the local copper deposition rate.

The NIST Curvature Enhanced Accelerator Coverage (CEAC) model of superconformal electrodeposition uses these parameters to predict filling of features. Most importantly, this model recognizes changes of local coverage of accelerator on the interface both by accumulation from the electrolyte and by changes of the local area upon which the accelerator has adsorbed. Accumulation of accelerator at the bottom of superfilling trenches is dominated by this geometrical effect. Accelerator coverage on the bottoms of

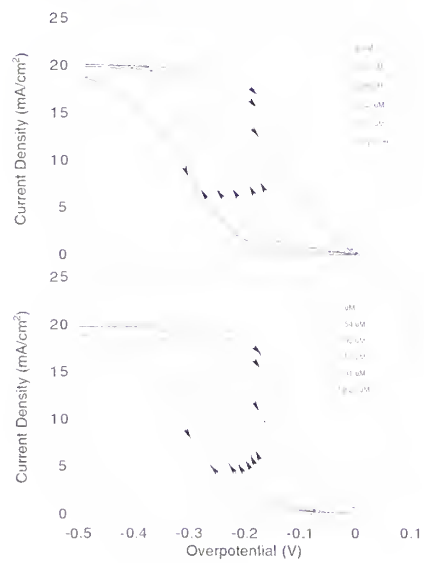



**Figure 1. (top) Experimental current-voltage curves for copper deposition on a flat copper substrate in electrolytes containing a deposition inhibiting additive plus varying amounts of an accelerating additive. Note the hysteresis and the saturation at high concentrations. (bottom) Fit of accelerator accumulation used to extract kinetic parameters for the Curvature Enhanced Accelerator Coverage (CEAC) model of superfill.**

fine features thus increases as the surface area decreases during copper deposition. This, in turn, accelerates copper deposition. The positive feedback cycle results in filling of the trench from the bottom upward, i.e., superconformal deposition. The finer the feature, the more important area change can be - it requires an appropriately designed electrolyte composition and appropriate deposition conditions to take full advantage of this effect.

This research, largely conducted in the past two years, has already resulted in accomplishments and impacts of consequence to the microelectronics industry. These include:

- Explained the significance for superconformal deposition of hysteresis in deposition on flat copper substrates.
- Showed how the hysteretic behavior can be modeled to extract kinetic parameters describing the rate and impact of additive accumulation on the copper/electrolyte interface. (Figure 1.)

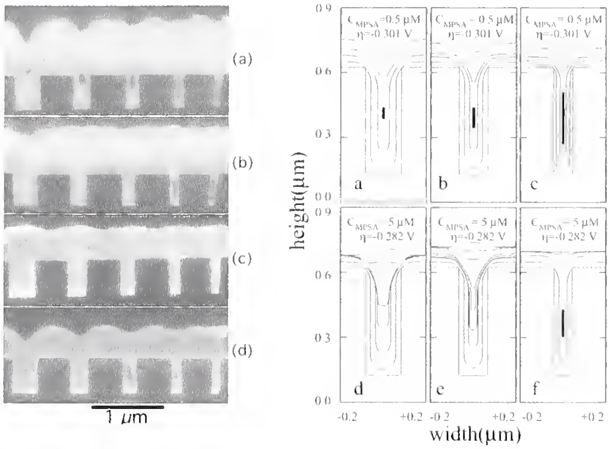



**Figure 2 (Left side) Superfill results for accelerator concentrations of (0, 0.5, 5 and 40) µmol/L (top to bottom). A window for superfill exists around 5 µmol/L concentration. (Right side) Predictions of the newest computer code for the three finest features at (0.5 and 5) µmol/L (top and bottom). Inclusion of diffusional effects results in voids indicating failure to fill. Simplifications in the first NIST model of superfill resulted in seams in features that failed to fill.**

- Developed the Curvature Enhanced Accelerator Coverage (CEAC) model that explains how accumulation of accelerator is impacted by changing area at the bottoms of fine features and how this effect causes superconformal deposition.
- Developed computer codes to predict superfilling of fine features using only the results of cyclic voltammetry studies with flat copper substrates. The most recent of these codes describes diffusion of the cupric ion and accelerator through the electrolyte, interface kinetics affecting transfer onto the copper/electrolyte interface, motion of the interface, and the impact of interfacial area change on accelerator concentration and local copper deposition rate.

This information has been conveyed to U.S. industry, academia and other national laboratories through eight presentations given in professional society meetings attended by industry representatives from electrolyte suppliers, analytical tool, plating tool and chip manufacturing industries.

In FY 2001 this work has also been disseminated through

- Refereed journal publications (3) showing the predictive power of the CEAC model by comparison of experimental filling results with model predictions. These publications are already being cited in the literature by industry and academia.
- Invited talks (2) at leading electrolyte and tool manufacturers.
- Industry-initiated collaboration with a major chip manufacturer.
- Mailing of publications to industrial and academic researchers in the field of copper electrodeposition (≈50).

In the coming year we will address several short and long term objectives:

- Examine the aspect ratio and dimensional fill limitations of the model electrolyte.
- Study additives for inhibiting and accelerating deposition of metals other than copper.
- Probe the generality of the CEAC model by studying superconformal deposition of metals other than copper.
- Disseminate modeling codes on the web page of NIST's Center for Theoretical and Computational Materials Science.

Through this work, researchers at NIST are providing the electrodeposition community with a better understanding of the mechanism by which organic addition agents lead to superconformal deposition of sub-micron features. It is anticipated that this will lead to the development of on-line monitoring tools that will allow industry to determine additive efficacy and consumption in commercial copper plating baths.

*"We are very excited about the capabilities of this tool, and we want to put it to use ASAP!!! Yet another example of NIST innovation helping industrial competitiveness!!! "*

— Dennis Buss, Vice President, Silicon Technology Development, Texas Instruments

*"This is exactly the kind of project where NIST can add to the fundamental understanding of our technology and help us all move forward."*

— Tom Ritzdorf, Director of ECD Technology, Semitool, Inc.

## For More Information On This Topic:

D. Josell, D. Wheeler, W. H. Huber, and T. P. Moffat, "Superconformal Electrodeposition in Submicron Features," Phys. Rev. Lett. **87**, 016102 (2001).

T. P. Moffat, D. Wheeler, W. H. Huber, and D. Josell, "Superconformal Electrodeposition of Copper," Electrochem. and Solid-State Lett. **4**, (4) C26 (2001).

T. P. Moffat, D. Josell, and Daniel Wheeler

# High Temperature Lead-Free Solders: Tools for the Microelectronics Industry

*Increasing global concern about the environment is bringing regulatory and consumer pressure on the electronics industry in Europe and Japan to reduce or completely eliminate the use of lead in most products. Worldwide, the microelectronics industry has made great progress toward application of lead-free solders in the relatively benign conditions of consumer electronics. In 2001, the National Center for Manufacturing Sciences (NCMS) completed the High Temperature Fatigue Resistant Solder Project to address the industrial need for lead-free solders in harsh environments, such as encountered in automotive under-the-hood applications. NIST played a leadership role in this research project, chairing the alloy task group and providing definitive, timely materials data and critical analyses needed for evaluating candidate solders, leading to the development of new lead-free solders with excellent performance, outperforming industry-standard compositions.*

Microelectronics assembly has, from its infancy, been based on tin-lead eutectic solder, a mixture of tin and lead that melts at 183 °C. In recent years there has been an increasing need within the avionics, telecommunications, oil exploration, and automotive industries for solders which perform reliably at ever-higher temperatures, temperatures which approach the melting point of tin-lead eutectic. Such harsh environment applications require solders with melting points higher than that of tin-lead eutectic in order to achieve the required reliability. In addition, recent legislative and marketing pressures in Europe and Japan have pushed U.S. manufacturers to pursue lead-free solders for all microelectronics applications, leading to the double challenge of developing high temperature, Pb-free solders.

In 1996, the National Center for Manufacturing Sciences (NCMS) initiated the High Temperature Fatigue Resistant Solder Project to address the need for high temperature, high reliability solders in response to a need identified and defined by a number of companies in the microelectronics, automotive, avionics and telecommunications industries.

The resulting consortium, consisting of eight industrial corporations, academia and NIST, has completed its four-year program. Consortium members include Allied Signal, Amkor Technologies, Delphi Delco Electronics Systems, Ford Motor Company, Heraeus Corporation, Indium Corporation, Johnson Manufacturing, Rockwell International Corporation, Iowa State University, and NIST. The goal of the project was to determine whether highly reliable, nontoxic, cost-effective substitutes could be found for high lead and Sn-Ag eutectic solders in harsh environments. This goal required gaining extensive knowledge of the properties and manufacturability of alternative solder alloys.

The project members initially identified about 200 candidate solder compositions. Experimental measurements on 52 of the alloys were made to characterize melting and wetting behavior and reactions with substrates during prolonged exposure at high temperature. A thermal-fatigue screening test was run on 12 of the most promising Pb-free alloys. From these candidates, 7 alloys were chosen for full scale manufacturing and reliability trials, utilizing a variety of surface mount components cycled up to 160 °C.

The project was divided into two major task groups – the Alloy Selection and Characterization Group and the Testing Group. In addition to chairing the Alloy Task Group throughout the project, NIST performed various other critical roles. As part of the initial assessment, NIST surveyed 12,000 binary and ternary metallic phase diagrams to identify eutectic compositions and congruently melting compounds with potential as candidate solder alloys. NIST had a leadership role in formulating the down selection criteria, and conducted the metallurgical analysis and metallography for the project. NIST also coordinated the

**Figure 1. Plastic leaded chip carriers on ceramic (top) and polymeric (bottom) substrates assembled with Pb-free solders and surface finishes.**

final analysis of the data, the determination of conclusions and recommendations, and the writing of the NCMS final report. The High Temperature Fatigue Resistant Solder Project was summarized in an invited article in Advanced Materials and Processes, April 2001, written by NIST staff. In addition, a technical paper presented by NIST was selected as one of the 5 best papers out of 58 presented at the TMS 2001 Annual Meeting Symposium on "Recent Progress in Pb-Free Solders and Soldering Technologies." This distinction included electronic

publication on the web through e-JOM as well as publication in the June issue of JOM journal (Journal of Metals). Major conclusions of the High Temperature Fatigue Solder Project are:

- Six lead-free alloy compositions were identified that exhibit fatigue performance during –55 °C to +160 °C cycling of a wide range of components which is superior to the industry standard eutectic Sn-Ag alloy.
- The seven lead-free alloys cycled with ball grid array (BGA) packages through 0 °C to +100 °C and –40 °C to +125 °C cycling all outperformed Sn-Pb eutectic solder.
- Manufacturing of these alloys and generation of solder pastes does not present any special problems.
- Present manufacturing equipment can be used to build assemblies in many cases.
- Alloy costs will not be a major factor .

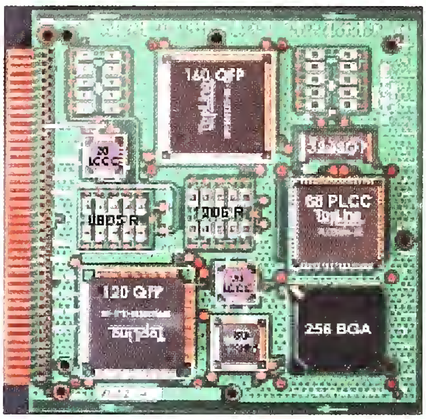



**Figure 2. Reliability Test Vehicle used to test manufacturability and thermal fatigue resistance of a variety of surface mount components on printed circuit boards.**

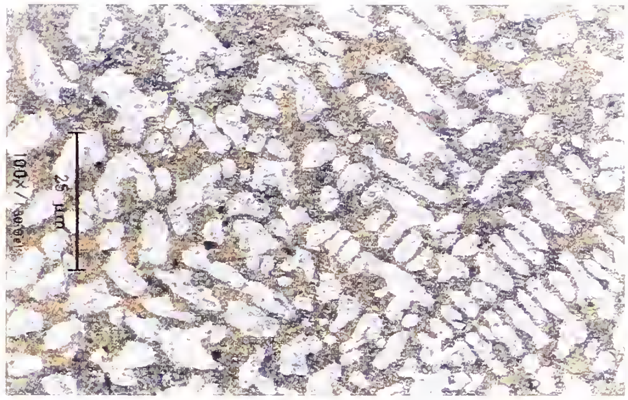



**Figure 3 Microstructure of an experimental alloy.**

"NIST personnel brought unique skills and expertise to both NCMS projects [the Lead-Free Solder Project, and the High Temperature Fatigue Resistant Solders Project]. Without the support from NIST, both these projects would have extended over a longer period of time and would have been more costly to the project's industrial partners."

— Duane Napp, NCMS Program Manager

## For More Information On This Topic:

NCMS High Temperature Fatigue Resistant Solder Project Final Report, NCMS, Ann Arbor, MI, 2001. Frank W. Gayle, "Fatigue-Resistant, High Temperature Solder," Advanced Materials & Processes 159 (4), April 2001, p. 43-44; Frank W. Gayle, et al., "High Temperature Lead-free Solder for Microelectronics," JOM, June 2001, p. 17-21.

# Process Modeling of Low Cost Powder Metallurgy Technology for Particle Reinforced Aluminum

*Major research efforts within the U.S. auto industry are driven by the need to reduce the weight of future vehicles to meet U.S. Council for Automotive Research (USCAR) and Partnership for a New Generation of Vehicles (PNGV) goals. This can most readily be accomplished by the substitution of lightweight materials for the heavy materials currently used. With the completion of this project, NIST has assisted industry in developing a low cost powder processing technology for aluminum alloy and particle-reinforced aluminum parts that may be substituted for iron-based powder metallurgy products. Efforts to mass produce acceptable parts using press-and-sinter and direct powder forging are underway. The NIST part of this effort focused on modeling each step in these consolidation processes from powder to fully dense part. Modeling provided a basis for rapidly designing successful processes.*

Reducing the mass of certain engine components, such as connecting rods and transmission fluid gerotor pumps, can have a large effect on engine efficiency and responsiveness far beyond the simple weight reduction. For this reason, these components were targeted by the U.S. Automotive Materials Partnership (USAMP) as candidates for their program on Low Cost Powder Metallurgy Technology for Particle Reinforced Aluminum. Currently, these components are produced from steel powder. NIST provided models of many of the various processes that had to be modified to switch to aluminum and these contributions are summarized here. Dr. John Allison of Ford and former Chairman of the USAMP Advanced Metals Division wrote of the NIST contributions, "The modeling effort … is an integral and very critical aspect of this program," and "[NIST's] impact could eventually extend well beyond this particular project."

In collaboration with the Micromechanics Centre at Cambridge University, a physically based constitutive law for consolidation of reinforced powder was developed. Its validity was tested at NIST on powders relevant to the USAMP program and found to accurately describe the consolidation behavior of reinforced powders. This model was implemented in a finite element model to predict the behavior of parts having complex shapes. USAMP funded a small business to develop the model for the specific shapes of interest to the program. The computer-modeling package is now available in a user-friendly, commercially supported form.

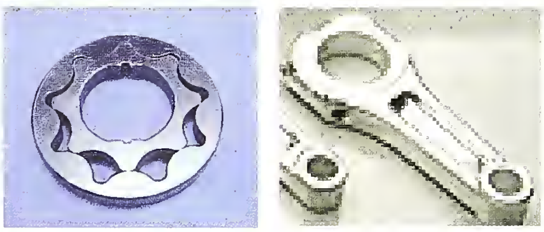


**Figure 1. Parts targeted by the USAMP project on Low Cost PM Technology for Particle Reinforced Aluminum.**

As part of the validation process, NIST developed databases for the materials of interest. These databases included the consolidation behavior of the various ductile phases as a function of temperature and the effect of various concentrations of reinforcement on this behavior. Additional modeling was carried out at NIST to provide guidance to the efforts. For example, one direction undertaken was to develop materials based on blends of soft, unalloyed aluminum powder with hard, alloyed powders. A natural question arose as to what minimum amount of unalloyed aluminum was needed to achieve a given level of density during cold pressing. The modeling approach was modified to provide some guidance and the nomograph in Figure 3 was the result. This particular figure predicts the

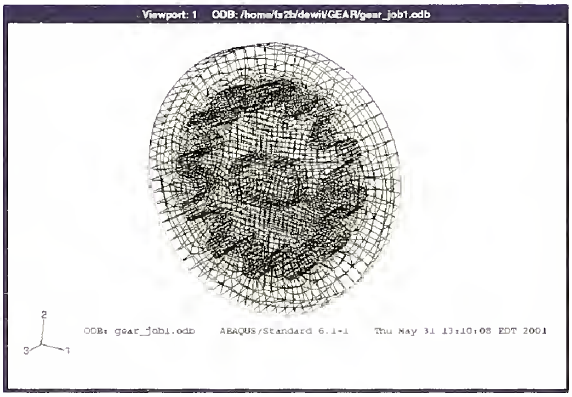




**Figure 2. Finite Element Model of Gerotor Die filled with powder that is modeled using the constitutive equation and data developed in this project.**

amount of aluminum needed to reach a relative density of 0.90 as a function of the size of the soft aluminum powder particles relative to the hard powder particles under a pressure of 620 MPa (45 tsi). The figure can be easily changed to address particular industrial requirements. It emphasizes the importance of particle size on the resulting behavior.

Another area in which process modeling helped was in sintering. In contrast to some other systems, sintering in powder metallurgy is carried out mainly to develop strength. No change in density is normally desired since this results in distortion or cracking. The modeling approach adopted for this project attempted to simply predict the time and temperature required

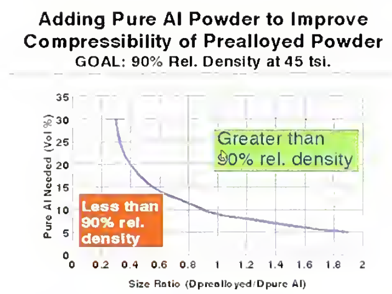




**Figure 3. Effective of pure aluminum on compressability of prealloyed powder.**

to homogenize the elemental blends into the intended alloy. Again, a strong dependence on particle size was found. This provided guidance to the powder suppliers as to what sieve sizes were desireable to blend to achieve homogenization on an industrial timeframe. NIST provided assistance to this project when an unexpected issue – powder flowability – stood in the

way of industrial implementation. Mechanical properties studies showed that these materials would only be successful if a relatively fine SiC powder were used as the reinforcement. NIST research showed that fine aluminum powders were required to be blended with such fine SiC powders. However, the resulting mixture would not flow down commercial feed tubes or through feed shoes into the dies for pressing. Using the Small Business Innovative Research (SBIR) program at NIST, modeling of powder flowability was carried out in conjunction with a small business. One outcome of this work was a means of using a gas to lubricate the powder particles and make flow possible.This technology was incorporated into the fluidized feedshoe shown in Figure 4. It has been used to make many sorts of powders flow from cosmetic and medicinal powders to ultrafine carbide

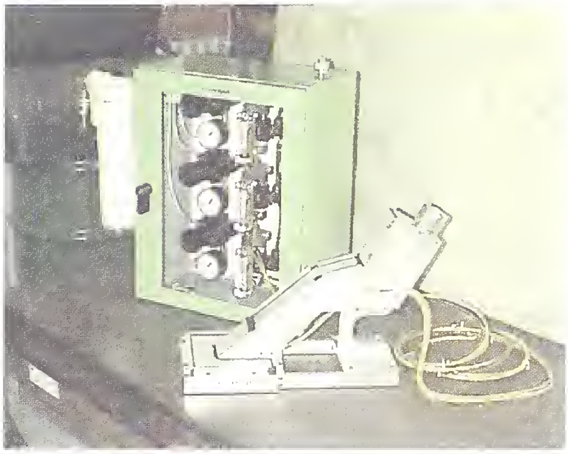


**Figure 4. Fluidized feedshoe and associated equipment for improving the flowability of fine or irregularly shaped powders into die cavities.**

powders for tools. The fluidized feedshoe is now commercially available from a powder press manufacturer as an accessory to their presses. It is being used by a number of U.S. companies to make parts using  fine powders or better parts using existing powders. One unexpected outcome of the technology is shown in Figure 5 – improved part uniformity. This figure shows the improved mass uniformity using the fluidized feedshoe. This mass uniformity translates into improved dimensional tolerances for PM parts.  It also permits more rapid feeding and increases productivity.

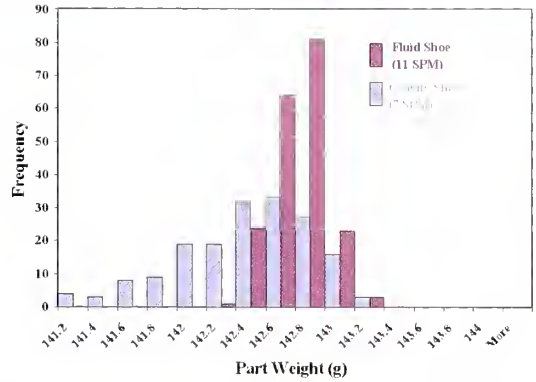



**Figure 5. Weight distribution for gears made with and without the fluidized feedshoe technology.**

## For More Information On This Topic:

R. J. Fields, T. Zahrah, and Y. Shim

# Standard Problems for Computational Micromagnetics

*Computational micromagnetic modeling is the dominant method used to calculate magnetization patterns and dynamics in materials and devices on length scales from nanometers to several micrometers. The demand for accurate micromagnetic modeling is accelerating as the industry wide trend of over 60% per year increase in bit density for hard disks creates increasing demands on our ability to predict and control the magnetization in materials and devices. Development of new magnetic devices including magnetic random access memory (MRAM) increasingly depends on the behavior of magnetization on nanometer length scales. Our activity in computational micromagnetics, started in 1995, is designed to facilitate testing of micromagnetic computer codes by specifying and publicizing a number of standard problems and then computing, collecting, comparing and publishing solutions to these problems.*

Micromagnetic modeling is used to compute magnetic domain structure and dynamics in magnetic materials starting from sample morphology, materials properties, and applied fields. This type of modeling is a very important part of device design, particularly for read heads in hard drives and magnetic random access memory (MRAM) cells. Micromagnetic modeling has also contributed a large amount to our understanding of recording processes and noise in magnetic recording media.

Our involvement in standard problems was designed to fill a need in industrial and academic labs for a method to check the accuracy of micromagnetic modeling software, usually developed independently in each lab, and tested by parts, energy term by energy term. Beyond finding "bugs" in software, the standard problems also provide benchmarks for modeling practice which can help to avoid errors introduced by overly coarse discretization, or loose convergence criteria.

The standard problems were one of two action items recommended in the initial workshop of the micromagnetic modeling activity group (μMAG) that drew approximately 100 attendees. This workshop was held as an evening session at the 1995 INTERMAG conference, and was sponsored by MSEL's Center for Theoretical and Computational Materials Science.

The standard problems were designed with the following criteria in mind:

- Geometries and materials properties should be similar to "real-world" applications.
- Specifications should be loose enough to allow different computational methods to be used, but tight enough to ensure that results can be meaningfully compared.
- The scope of the problem should be small enough that it would not be too expensive in manpower or computational time to compute a solution.
- The problems should be significant enough to allow solutions to be published in the usual scientific journals.

The specifications for the standard problems presented below were all written by NIST, based on suggestions received from members of the micromagnetic modeling community. Solutions to these problems were calculated by NIST and by contributors from across the globe. Detailed specifications and results are available on the μMAG website:

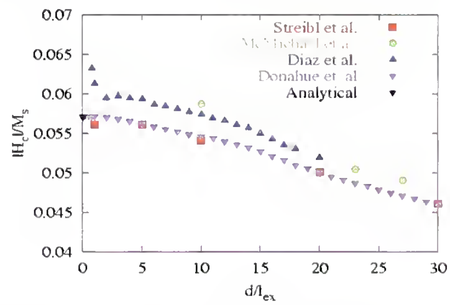
http://www.ctcms.nist.gov/~rdm/mumag.html

Standard Problem #1 is a 1 mm x 2 mm x 20 nm rectangle of material with properties to mimic Permalloy, and the requested results are hysteresis loops and magnetization patterns obtained at zero applied field. When the first few submitted results were found to have wide disagreement, we quickly decided to protect the contributors by collecting results anonymously. Nine solutions were collected and posted on the mMAG website with widely varying results. While Standard Problem #1 may be regarded as a failure regarding its use in checking micromagnetic software, it remains important as the first attempt at a public standard problem in micromagnetics, and as a computational challenge.

Standard Problems #2 and #3 were developed from discussions at a second μMAG workshop held as an evening session of the 1998 Joint MMM-INTERMAG conference.

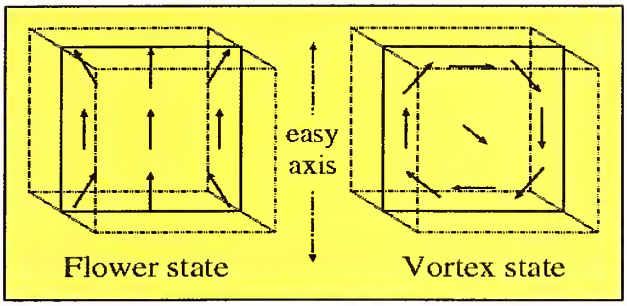
Standard Problem #2 is a variable-sized bar of material with aspect ratios of 5:1:0.1. All lengths are expressed in units of the magnetostatic exchange length, which is a function of the material exchange stiffness constant and the magnetization. The results collected for comparison are the coercive field and the remanant magnetization as a function of the width of the rectangle.

Four solutions for Problem #2 have been collected and posted on the μMAG website. Three of these results were first presented at the MMM'99 conference in a special evening session on micromagnetic standard problems. The attendees, numbering more than 100, were delighted to see good agreement between results calculated independently and by different methods. The fourth Problem #2 result is our revision of our earlier result and an analytical result for the coercivity in the limit of a small particle.



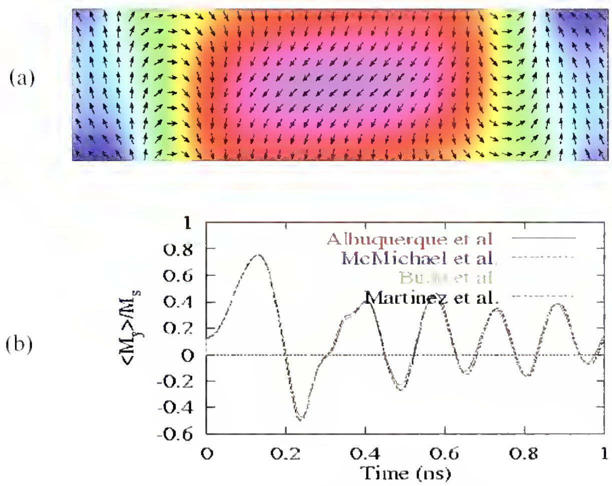

**A comparison of coercivity values calculated for Standard Problem #2.**

Standard Problem #3 is specifically designed for 3-D calculations. The object is to calculate the minimum energy magnetization configuration for a cube of material with some uniaxial anisotropy. For small cubes, the minimum energy configuration is a "flower" state, and for larger cubes, the expected minimum energy state is a "vortex" state. The result collected for comparison is the critical length of the cube edge for which the energies of the two states are equal. One of the submitted results revealed a surprise "twisted flower state" which has lower energy than either the flower state or the vortex state.




**Diagrams of the flower state and vortex state from the specification for Standard Problem #3.**

Standard Problem #4 is designed to test dynamic calculations based on Landau-Lifshitz-Gilbert equations of motion. The details of magnetization dynamics are becoming more important for magnetic recording as data rates increase, and for MRAM development, the details of switching behavior are critical. In Problem #4, switching is calculated for a 500 nm x 125 nm x 3 nm rectangle of Permalloy starting from an equilibrium state in zero applied field. One of two specified applied fields are turned on to induce switching, and the magnetization dynamics are traced as a function of time. For one applied field, the magnetization rotates in the same direction everywhere in the sample, but for the other, the switching is more complicated, with rotation starting in one direction near the ends of the bar and in the other direction in the middle.




**Snapshot of the magnetization during reversal (a) and (b) magnetization dynamics from Standard Problem #4.**

These micromagnetic standard problems provide computational physicists and engineers in industry and academia with benchmarks for micromagnetic software development and micromagnetic modeling practice. By assuming a leadership role in the field, by providing standard problem specifications and by providing electronic access to submitted solutions including our own solutions, we have raised the quality of micromagnetic modeling, and we have provided a means to assess the reliability of micromagnetic modeling results for modelers and for their customers. NIST could not have made these standard problems without the contributions of colleagues across the globe, especially in Europe, who computed and provided solutions to the standard problems.

## For More Information On This Topic:

Standard Problem specifications and results are published on the μMAG web page: http://www.ctcms.nist.gov/~rdm/mumag.html

R. McMichael, (NIST/MSEL) and M. Donahue and D. Porter (NIST/ITL)

# Particle Temperature Measurement Issues for Thermal Spray Processing

*Temperature and velocity measurements of particles and droplets provide important process parameter data for modeling and control of the Thermal Spray (TS) coating process. Accurate measurement of particle temperature using non-contact temperature sensors depends on the use of appropriate sensor calibration procedures. In this project completed this year, we demonstrated several methods for calibrating two-color optical pyrometers including a high temperature blackbody and a tungsten ribbon standard lamp as calibration sources. Comparing the different methods shows that the absolute temperature and wavelength-dependent emissivity of any non-blackbody calibration source must be well known to obtain an accurate sensor calibration. Further, emissivity data on individual heated particles were shown to improve the accuracy of particle temperature measurement by two-color pyrometry.*

In the air plasma thermal spray (TS) process for producing coatings, solid particles are injected into and heated by a plasma jet. From the beginning of the injection process through interactions with the plasma jet, the particles will have wide ranges of temperatures, velocities and trajectories that then translate into a microstructure as the impinging particles solidify to form the coating layer. Particle diagnostics within the TS plume are favored as a means of improving process reproducibility because they yield information on both the physics of the coating process itself and the process variability. TS particle sensors fill two roles. They are used in quality control operations to "tune" thermal spray torches to ensure consistent coating deposition. They are also widely used in thermal spray research, including developing parameter sets for new spray materials, evaluating improved spray torches, and studying relationships between processing conditions and coating properties. Such diagnostics make rational process improvement possible, a difficult endeavor when only process settings, such as torch power or gas pressures, or a final coating property can be measured.

These important particle data are provided by non-contact optical temperature and velocity measurements from sensors and software that process light intensity readings from particles within the TS plume. Two-wavelength ratio pyrometry is usually employed for measuring particle temperatures because it is insensitive to particle size, absolute emissivity and particle position within the sensor field of view. It requires only that the particle emissivity not vary over the operating wavelengths of the sensor, known as the graybody assumption. Several approaches are now available: 1) Single particle, non-imaging sensors that collect data one particle at a time and average the results from several particles at the same location or, by moving the sensor position, within a defined area; 2) Particle ensemble, non-imaging techniques that acquire data related to some average temperature and velocity of the particle stream; and 3) Imaging pyrometry that measures multiple individual particles simultaneously by focused imaging of a large volume of the spray plume. Temperature measurement using these optical techniques requires a calibration procedure to provide the appropriate coefficients for conversion of the measured light intensities to temperature values.

In the last few years NIST has been working to assess industry needs and address several of these non-contact temperature measurement issues. Industry needs have been determined by reviewing published papers and reports, discussions with colleagues, and through workshops (several sponsored by NIST) focused on issues related to the TS coating industry. At the Workshop on Non-Contact Thermometry held at NIST in October, 2000, the importance of absolute temperature measurement and traceability for industrial applications was discussed. At the recent workshop on Thermal Spray Process Reliability held at NIST in January, 2001, the consensus was that the reproducibility and reliability of TS coatings need to be improved in order to realize the full benefits of this technology.

As a possible solution, representatives of industry and academe expressed interest in combining process measurements with coating property data into an integrated database that would provide guidance in the use of thermal spray technology to coating developers and potential users alike. Their hope is that improved process measurements, coupled with increased awareness of thermal spray as a well-understood means for enhancing surface properties and synthesizing novel materials will expand its broad-based benefit. A report is available that includes the workshop presentations and discussions (NISTIR 6776.)

During the Thermal Spray Process Reliability workshop, specific questions were raised concerning the calibration of particle temperature sensors, and how the properties of the particles being measured (e.g., composition, oxidation, etc.) affect the accuracy with which temperature is determined. In response, the Metallurgy Division has taken steps to outline recommended calibration procedures for thermal spray particle temperature sensors and to provide particle emissivity data for improving temperature measurement accuracy.

Current work on calibration procedures has involved evaluating the use of tungsten standard ribbon lamps as calibration sources for two-color pyrometers. Tungsten lamps are used because they are readily available, but because of their deviation from graybody behavior they are not as suitable as an ideal blackbody calibration source. Errors caused by the deviation from graybody behavior are shown in Figure 1. They can be corrected using tungsten emissivity data available in the literature, or by direct measurement of the emissivity of the lamp by spectroscopy.

An additional calibration issue involves the fact that tungsten lamps are typically calibrated to serve as radiance temperature standards. These lamps are appropriate for calibrating single-color but not two-color pyrometers. The reason is that the radiance temperature scale, which is defined for a perfectly radiating surface (e.g., blackbody, $\varepsilon = 1$), is meaningful only at the calibrated wavelength of the lamp, and therefore it cannot be transferred to a pyrometer that operates at two wavelengths. Absolute temperature of the filament must be determined and used instead. Radiance temperature can be converted to absolute temperature using the normal spectral emissivity of tungsten at the lamp wavelength. Though easily addressed, this error is often overlooked, resulting in serious systematic errors in particle temperature measurements. Figure 2 shows the errors incurred using radiance temperature rather than absolute temperature in the calibration of a generic two-color pyrometer. The accuracy of

these corrections using literature data is evaluated by comparing the resulting calibration to calibrations obtained using a black-body.

With the transfer of these results throught the technical literature, our project on Thermal Spray Processing has now been successfully completed.

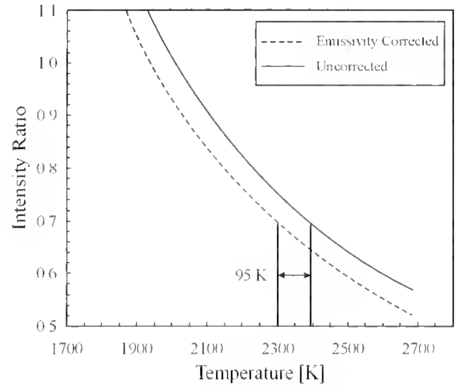



**Figure 1. This figure shows the effect of the deviation from graybody behavior of the calibration source for a two-color imaging pyrometer.**

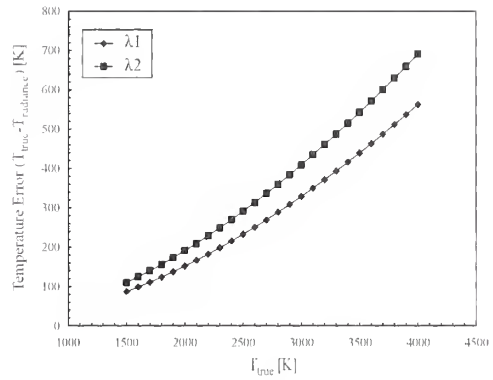



**Figure 2. This graph shows the error associated with the use of radiance temperature rather than true temperature in the calibration of a generic two-wavelength pyrometer operating at λ1 = 700 nm and λ2 = 900 nm. The calibration source has a normal spectral emissivity of ε = 0.43.**

## For More Information On This Topic:

S. D. Ridder, *Thermal Spray Process Reliability: Sensors and Diagnostics*, NISTIR 6776, August, 2001.

S. D. Ridder, F. S. Biancaniello, S. P. Mates, and R. D. Jiggetts (NIST/MSEL)

# NIST Research for Springback Predictability and Sheet Metal Forming in the Auto Industry

*Market and regulatory pressures are driving the automotive industry to develop and use new materials and manufacturing methods while competitive pressures are forcing them to keep costs low and reduce the time required to bring a new vehicle from concept to market. Current automotive production technology has evolved around stamping of relatively low strength steel to form automotive body panels and components. While this approach was acceptable when designs and materials were not changing dramatically, this process of die design and tryout may limit U.S. automakers' abilities to utilize new materials in their designs or to bring a new design rapidly to market. NIST has been working with the automotive industry to improve the die design process and reduce die development and tryout costs.*

One area that has long been a concern to the auto industry, but has become a major concern due to the increasing pressure to use lighter materials and reduce die development time and costs, is springback. When the material being formed is a low strength material, springback from the die face following stamping will be relatively small and can be accounted for by experience and during die tryout. This sitation is no longer the case - new, higher strength steels and aluminum alloys have greater springback magnitudes; designs of increased complexity are often accompanied by unpredictable springback magnitudes and directions; and demands continue for reduce time to market. These factors point to the need for spingback to be addressed earlier in the die design, development and tryout process.

The industry thus needs better predictive models based on a sound fundamental understanding of springback phenomena and appropriate measurements, standards, and data. In response to this need, a consortium of aluminum and steel producers, a software company, and the three automotive manufacturers and their suppliers received support from NIST for 5 years to develop finite element software that can predict springback. The resulting ATP Springback Predictability Project (SPP) greatly reduced the uncertainty in springback predictions by finite element models and brought a higher level of understanding of springback to the sheet metal forming industry. The ATP/SPP concluded in October 2000.


**Figure 1. Plaque given to NIST staff that presented research results to SPP during the ATP funded phase.**

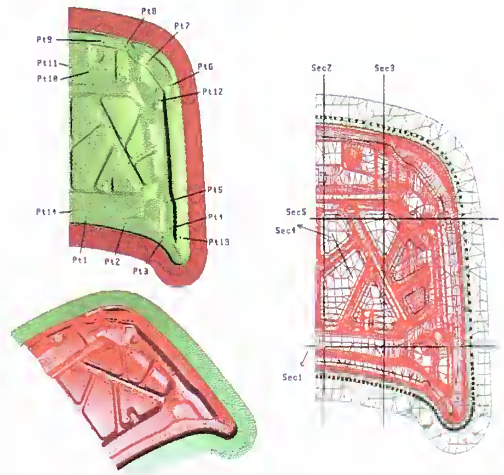



**Figure 2. The inner panel of a car hood was one of the components targeted by industry for in-depth investigation of its springback behavior.**

The Metallurgy Division was involved with this project from its beginning, carrying on a set of parallel, non-proprietary research projects complementing SPP activities. There were three projects: fundamental dislocation studies, deformation-induced surface roughening, and standard test methods. The most significant contributions by these projects to a deeper understanding of springback and forming in general were:

- A model based on percolation theory was derived to describe and predict the movement of dislocations through a work-hardened microstructure.
- Analyses and experimental measurements demonstrated the importance of anelastic effects in plastic deformation and springback.
- A new experimental technique, ultra small angle x-ray scattering (USAXS) imaging, was shown to hold promise as a useful tool for studying dislocation structures *in situ*. When a USAXS scan is made, the data are in the form of a slit-smeared scan through a single-direction in reciprocal space. Once a scan is made, interesting features can be identified and the analyzer crystals can be set to a specific location on the scattering curve. The sample can then be imaged *through* the analyzer stage. What makes this technique potentially useful is that USAXS imaging can select weak scattering components (such as dislocations) and form the image from just these components.

- The influence of microstructural and compositional differences on the roughening rate during uniaxial straining was determined. A generic model for deformation-induced surface roughening was developed.
- A biaxial test facility was set up at NIST to generate well defined multiaxial strain states to simulate forming conditions and develop standard measurement methods.
- A well attended conference on the fundamentals of dislocations and plasticity was held at NIST to provide U.S. industry with the most up-to-date science.

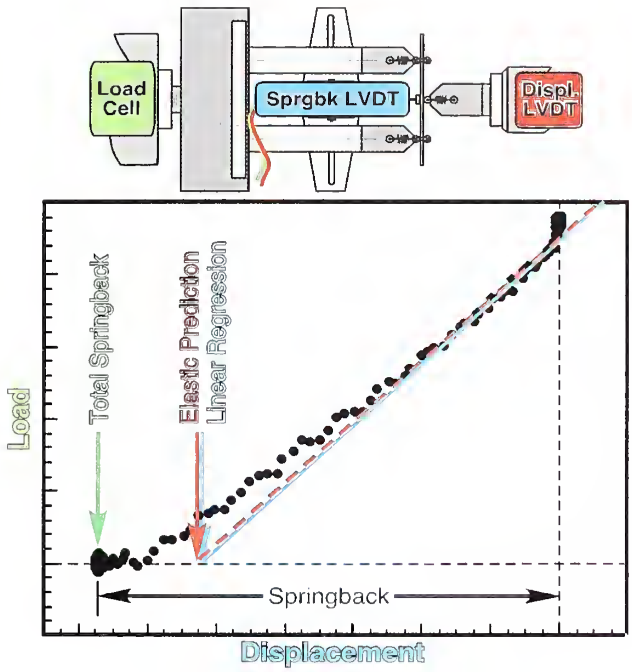



**Figure 3. Springback measured in 3-point bend showing linear and non-lined components.**

The Springback Predictability Project and joint venture partnership was considered so successful that industry decided to continue its activities with their own funds after ATP support ended. A poll was taken of the industrial members to decide the assignment of priorities to a list of 17 activities. Continued interaction with the NIST forming research effort was ranked second highest in priority.

NIST has responded to this request from industry. The three projects that arose from the initial industrial interaction form the basis of the Forming of Lightweight Materials Program described in this Annual Report of the Metallurgy Division. Some specific actions to address the industrial needs are:

- The conclusion that anelastic recovery may be able to account for this remaining uncertainty was well received by the SPP members. To enable obtaining a better understanding of the role of anelastic deformation in springback and dislocation dynamics in surface roughening, a dynamic mechanical analyzer was purchased. This system is capable of testing mechanical testing at frequencies up to 200 Hz and temperatures from (–150 to 600) °C with a strain resolution of 1.0 nm. This system can be used for dislocation damping (internal friction) measurements, creep, stress relaxation measurements, and anelastic strain recovery measurements. This system will enable NIST to relate fundamental dislocation structures and dynamics to the deformation behavior important to the forming industry.
- We will participate in two other industry-led consortia: Warm Forming of Aluminum and Active, Flexible Binder Program for Metal Stampings. Our involvement will be to investigate the elevated temperature formability of sheet metal by upgrading our biaxial tester to carry out tests on heated metal. The role of roughening on friction will also be pursued to improve predictability.

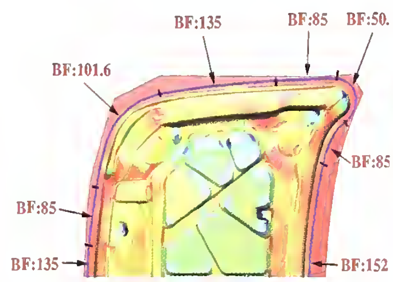



**Figure 4. Inner panel of car hood.**

**For More Information On This Topic:** R. J. Fields, T. Foecke, L. E. Levine, and R. E. Ricker (NIST/MSEL)

# Thermodynamic and Kinetic Modeling of Multicomponent Alloys

*Commercial alloys rarely consist of only two elements and some contain up to 10 elements. In addition, many important industrial processes rely on diffusion to control the formation and dissolution of precipitate phases within a matrix or at an interface. The development of thermodynamic and diffusion databases enables the extrapolation of these properties from binary and ternary systems to needed higher order systems. NIST's development of such databases for Ni-base superalloys allows the modeling of various processing applications. The approach has been shown to give reasonable predictions for complex alloys and provides a compact storage method for vast quantities of data.*

During the last decade, researchers from the Metallurgy Division have collaborated with scientists from universities and industry on several projects with emphasis on modeling tools for the design and manufacture of superalloys. Structural parts made from superalloys not only must withstand extended periods of service at high temperatures, but also must tolerate severe environmental conditions, such as highly corrosive fumes from a jet engine. In addition to the increased performance required for aerospace applications, the performance demands for land-based energy applications are also increasing. The traditional approach for development of a new alloy relies on the knowledge and experience of the engineer, which can be costly due to the significant amount of testing required to obtain the correct properties.

Two projects, the NIST-sponsored Consortium on Casting of Aerospace Alloys and the DARPA-sponsored Investment Casting Cooperative Arrangement, focused on the modeling of casting processes. For these projects, the Metallurgy Division developed phase equilibria subroutines, which used a modified version of public domain software code, and constructed a thermodynamic database for Ni-based alloys. On the basis of these subroutines, programs were developed that perform equilibrium (lever) and Scheil solidification calculations for multicomponent alloys. UES Software, Inc., implemented these codes into ProCAST™, a finite element method software package for the simulation of casting processes. The original NIST Ni-superalloy thermodynamic database includes 9 elements, Ni-Al-Co-Cr-Mo-Re-Ta-Ti-W, and is based on critically evaluated literature work and NIST work on Co-Mo, Co-Ti, Co-Re and Re-Ti systems. Figure 1 shows the results of the assessment of the Co-Ti system. This database includes all known phases in this 9-component system. Recently, the description of the liquid, $\gamma$, and $\gamma'$ phases were expanded to include Hf. Electronic versions of the NIST database have been distributed to various industries, universities, and national laboratories.

As a result of this work, the detailed solidification behavior for Ni-base superalloys can be predicted. This has improved the quality of solidification simulations for investment castings, by providing more reliable predictions of casting defects, and thus allows industry to eliminate the need for extensive testing of many castings to reach an acceptable design.

In addition to a dependence on multicomponent thermodynamics, a wide variety of Ni-base superalloy applications are made more complex by diffusion processes, including solidification, homogenization, $\gamma'$ precipitation, bonding and repairing processes, and protective bond coats. Many of these industrial problems can be addressed using a commercial finite-difference diffusion simulation code that incorporates composition-dependent diffusivities combined with multicomponent

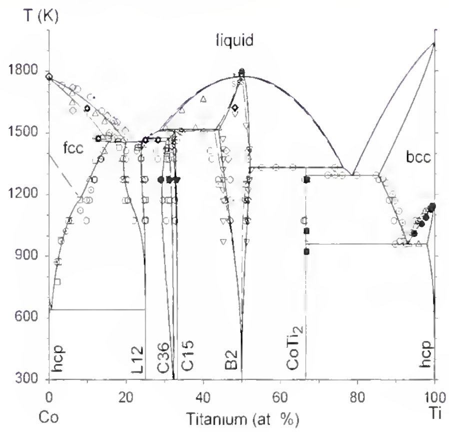



**Figure 1. The assessed Co-Ti phase diagram (lines) compared to selected experimental data (symbols)**

thermodynamics. The first step in modeling these multicomponent multiphase diffusion problems is the development of a multicomponent diffusion mobility database. This database is used in conjunction with the developed thermodynamic database to calculate the composition-dependent diffusivities for a given phase. As part of a General Electric-lead DARPA project for Accelerated Insertion of Materials (AIM), NIST is developing a diffusion mobility database for Ni-base superalloys. The NIST mobility database can be used in conjunction with the NIST Ni-superalloy thermodynamic database, as well as other commercial thermodynamic databases.

The diffusion data in various constituent binary systems have been assessed to establish this multicomponent diffusion mobility database. The initial diffusion mobility database is focused on substitutional diffusion in the $\gamma$ (fcc) phase for the Ni-Al-Co-Cr-Hf-Mo-Nb-Re-Ta-Ti-W system. The mobilities determined for the self-diffusion of the components in the metastable fcc phase (where applicable) are consistent with the well-known correlation of melting point and diffusivity. The general agreement of calculated and measured diffusion coefficients in the Ni-Co-Cr-Mo and Ni-Al-Cr-Mo systems demonstrates the validity of the database for the extrapolation to higher order systems.

The current diffusion mobility database has been distributed electronically to various industrial partners who are evaluating the database and providing additional experimental data for further validation of the database. One such validation, which is in progress, compares the simulation diffusion profile between two commercial Ni-base superalloys in the single-phase $\gamma$ (fcc)

region with experimental results. Figure 2 shows the composition profiles predicted from a diffusion couple simulation using the current mobility database.

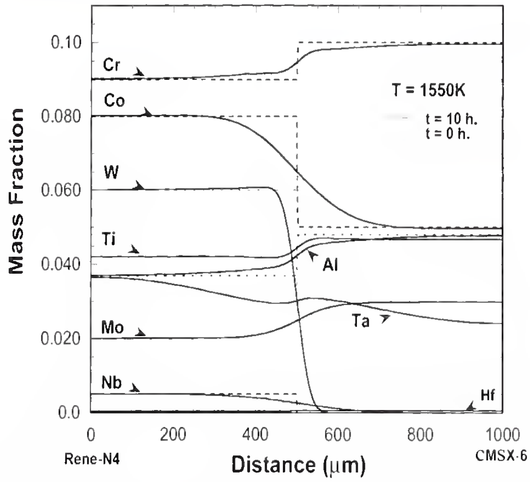



**Figure 2. Composition profiles predicted for a diffusion couple of René N4 and CMSX-6 superalloys in the single-phase γ (fcc) region at 1550 K for 10 h.**

In addition to the prediction of diffusion profiles between commercial superalloys, an approach that combines multi-component thermodynamics and diffusion is being utilized to determine the γ' particle size and γ' particle size distribution that is obtained after solidification and heat treatment. Also, diffusion simulations can be used to optimize the heat treatment schedules for cast superalloys to avoid incipient melting while minimizing cost. Further advancement of multicomponent multiphase diffusion simulations includes modeling the diffusion in the ordered γ' phase and development of a more user-friendly electronic diffusion database for public use.

NIST's work on multicomponent thermodynamics and diffusion has been widely recognized by various forums including:

- The 1998 Award for Excellence in Technology Transfer by the Federal Laboratory Consortium for "Transfer to the Aerospace Industry of Technology Developed for use in the Analysis of Advanced Casting Processes" (together with other researchers from MSEL and CSTL) .
- The 1999 Department of Commerce Gold Medal and the 2001 TMS Bruce Chalmers Award were both bestowed on W. J. Boettinger, partly for his work in solidification research.
- The paper "Thermodynamic Assessment of the Co-Mo System" was awarded the 2001 Alloy Phase Diagram International Committee Award for outstanding evaluation of phase equilibria data.

"The efforts of NIST researchers on the Cast Aerospace Alloys consortium were instrumental in making solidification science available to the foundry floor. Their efforts on developing a thermodynamic database for Ni-base superalloys and coupling it with solidification pathway analysis, thermophysical property measurements, spurious grain formation studies, and solid/liquid interface sensors have significantly increased our understanding of solidification in the investment casing process. The success of these activities is paving the way for additional collaborations with important commercial benefit to Howmet."

— Boyd A. Mueller, Howmet Research Corporation

## For More Information On This Topic:

"Development of a Diffusion Mobility Database for Ni-Base Superalloys", C. E. Campbell, W. J. Boettinger and U.R. Kattner, Acta mater, *in press*

W. J. Boettinger, C. E. Campbell and U.R. Kattner (NIST/MSEL)

# Forming of Lightweight Materials for Automotive Applications

Automobile manufacturing is a materials intensive industry that involves about 10% of the US workforce. In spite of the use of the most advanced, cost effective technologies, this globally competitive industry still has productivity issues related to measurement science and data. Chief among these is the difficulty encountered in die manufacture for sheet metal forming. In a recent ATP sponsored workshop (The Road Ahead, June 20-22, 2000, at U. S. Council for Automotive Research (USCAR) Headquarters), the main obstacle to reducing the time between accepting a new design and actual production of parts was identified as producing working die sets. This problem exists even for traditional alloys with which the industry is familiar. Figure 1 shows an example where the cost of tooling (dies) is the largest single cost in the production of parts for small cars. (This does not include assembly costs.)

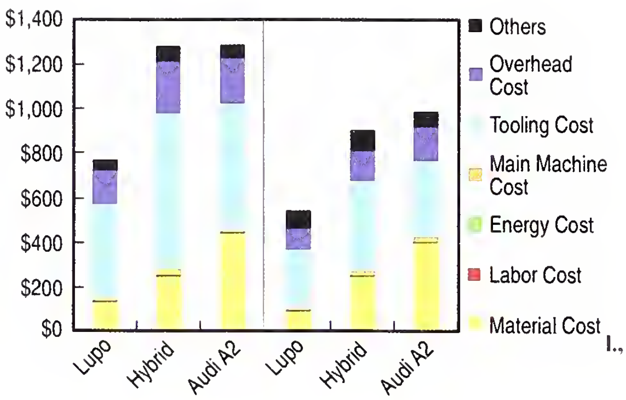



**Figure 1. Part cost breakdown for small cars. (Kelkar et al,. J. of Metals, pp 28-32, Aug 2001.)**

To benefit from the weight saving advantages of high strength steel and aluminum alloys, a whole new level of formability measurement methods and data is needed, together with a better understanding of the physics behind metal deformation. This project is meeting the industrial needs (see Table 2) by developing standard formability test methods, multiscale, physically-based constitutive laws, and models for consolidation of aluminum matrix composites. In the past year, we have established a sheet metal formability laboratory. A state-of-the-art formability testing machine equipped with an advanced surface displacement analysis system permits us to investigate industrially important measurement problems in formability and pursue standard test methods for formability. The facility provides test samples of biaxially deformed metal for other aspects of this program. For example, deformation-induced surface roughening of sheet metal is a poorly understood phenomenon that is highly relevant to industry. We are currently performing controlled experiments on biaxially strained sheets to develop a surface roughening data base and a generic model which industry has identified as a high priority need.

| Industry Need | NIST Solution |
|---|---|
| Improved finite element models for die design | Multiscale, physically-based constitutive relations |
| Known workpiece/die friction and high quality surface finish | Generic model of deformation-induced surface roughening |
| Materials properties that correlate with forming performance | Standard test methods for measuring formability |

**Table 1. Industry needs being met by NIST solutions.**

On a more fundamental level, we are using MSEL's advanced characterization capabilities such as transmission electron microscopy, synchrotron radiation, and neutron scattering at the NIST National Center for Neutron Research to understand the basic dislocation patterning responsible for the observed behavior of metals. A predictive model based on percolation theory has been developed from the measurements and observations. All aspects of the research at NIST will impact our customers by improving the commercially available, finite element computer codes that are heavily used by this industry. A key element in the design of this program is that an insight or advancement gained in one area can be immediately used in a piecewise fashion in the design process, i.e., total success of the program is not required to have an impact. Other means of transferring this technology, such as through standardizing organizations and by direct interaction with industrial counterparts, are being pursued. While targeting the auto industry, our research will have extended applications to all other industries that employ metal forming in their production lines.

**Contact Information: Richard J. Fields**

# Standard Test Method Development for Sheet Metal Formability

Tim Foecke and Stephen W. Banovic

*In order to meet its goals for fuel efficiency, the U.S. automotive industry is moving to lighter, high strength materials for auto bodies. However, their lack of experience in forming these materials translates into difficulty in making accurate dies for producing body parts. Through a survey of the U.S. auto industry, NIST identified a critical need to provide designers with accurate material properties and with a way to incorporate them into finite element models of sheet metal forming dies. This project seeks to develop new standard tests and metrology to accurately determine sheet metal mechanical response under forming conditions.*

In order for the U.S. auto companies to be able to transition to new materials for formed sheet metal parts, they must be able to mechanically characterize the starting materials under forming conditions, and input this information into die design models. The Metallurgy Division has initiated a project intended to develop a sheet metal formability test, along with associated metrology, that can be standardized and easily used by industry.

Our research has focused on a modified Marciniak geometry bi-axial tension test. By modifying the geometry of the blank and washer, we are able to produce strain states that vary continuously from balanced biaxial through plane strain to nearly drawing conditions. Using this testing scheme, one can produce an in-plane forming limit diagram (FLD) using a single tooling set and machine. One eventual goal of this project is to develop the methodology to measure an unambiguous multiaxial stress-strain curve in sheet metal. An image correlation software package is being tailored to measure the entire strain response, and several techniques are being investigated to directly measure the stress in the sample. If successful, these techniques combined will allow the first clean measurement of a multiaxial stress-strain curve.

Current work is investigating the uniformity of biaxial strain states for a given blank and washer geometry, the effect of strain rate on uniformity and strain state, and the effect of burrs and defects on premature localization. The plot shows the results to date in attempting to duplicate the published forming limit curve in 5052-H32 aluminum. Measured limit strains are consistently below those reported previously, but follow an identical trend. This is due to the fact that most published FLDs have been produced using simulative experiments such as the limiting dome height (LDH) test, in which the sample experiences out of plane bending and unquantified frictions during deformation. Our modified Marciniak test is intrinsic, in that it is testing the real properties of the sheet and is not limited by these experimental artifacts. Our results show lower limit strains because we do not have friction-stabilized instabilities on the surface and because we are testing a much larger area in a given strain state, and sample a larger population of defects. We have also modified the basic plane-strain configuration to increase the uniformly strained area. The result is shown below, along with a plot of the minor strains (avg. of 10 runs), acceptable values colored blue. The typical uniform area in the old geometry is traced in black. Using this new geometry, we are able to test a much larger area of material, and get a more accurate intrinsic plane strain limit.

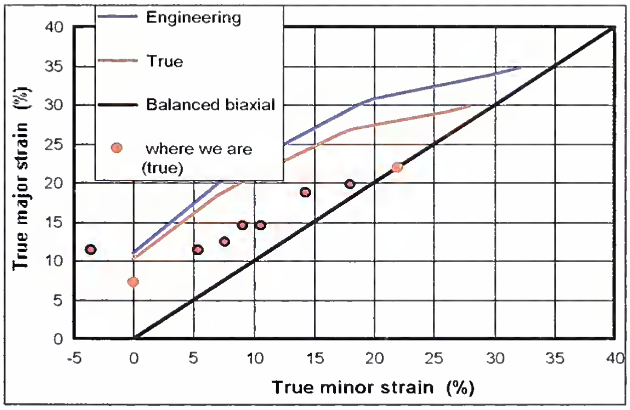



**Figure 1. Forming Limit Curve comparing LDH and NIST experimental values.**

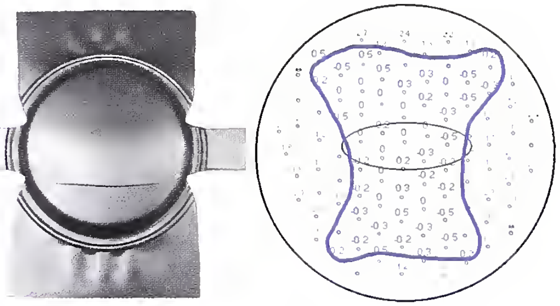


**Figure 2. NIST plane-strain geometry and uniformity plot.**

Samples produced by this project are used in other facets of the formability program to study friction, surface roughening and texture changes as a function of strain state and history in a number of sheet metal material systems. These parameters are all needed for accurate modeling of sheet metal forming.

## Contributors and Collaborators:

R. deWit and Y-W. Chung (NIST/MSEL), W. Tong (Yale University), and Y. Xu (Ford)

# Surface Roughening and Homogeneity of Plastic Deformation

Richard E. Ricker, Mark R. Stoudt, and Stephen W. Banovic

*The automotive industry has found that lightweight aluminum alloys do not deform as homogeneously as currently used alloys. In addition, an industry consortium determined that existing measurement methods, data, and knowledge of surface roughening mechanisms, friction, and wear were insufficient to meet their finite element modeling needs. To fulfill this need and enable greater application of energy efficient lightweight alloys, this project examines the metallurgical factors that influence the distribution of slip, friction, and wear during forming and quantifies these processes for use by the metals forming industry in finite element codes.*

During FY2001, research was conducted in four different areas: (i) uniaxial tension, (ii) forming friction, (iii) biaxial tension, and (iv) springback. Uniaxial tension experiments are used to evaluate specific hypotheses on the influence of metallurgical variables on surface roughening during deformation. This year, experiments into the influence of grain size on the roughening rate of a commercial aluminum alloy (AA 5052), initiated in FY2000, were completed. Although this work found that grain size strongly influences roughening rate, commercial Al alloys such as 5052 contain second phases at grain boundaries that influence deformation and limit grain growth. Follow-up studies were initiated to measure the influence of grain size on roughening of a high purity Al-Mg binary alloy without these particles and of a steel alloy where a wide range of grain sizes can be investigated.

The metallurgical factors that determine friction during forming and the relative importance of surface roughness and deformation character are unclear. Static friction experiments were performed on AA 5052 with different amounts of strain induced roughness to determine the influence of initial roughness on friction when there is minimal contact induced deformation. These experiments found that the coefficient of static friction initially increased and then decreased for these conditions, as shown below. To enable measurement of sliding friction over a range of contact induced deformation volumes and sliding velocities, a system for the measurement of sliding friction was designed and fabricated for mounting on a servo-hydraulic testing machine. Initial experiments indicate that this system will enable measurement of frictional forces over a wide range of conditions relevant to the forming industry for evaluation of die wear mechanisms.

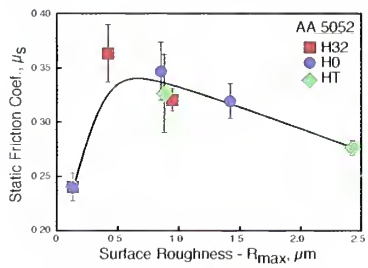



**Figure 1. Static friction for surface roughnesses generated by plastic strain.**

Since most forming operations involve complex loading conditions, the NIST metal formability testing machine was used to evaluate surface roughening rates in biaxial strain. This research found that the orientation dependence of roughening rates observed in uniaxial tension disappears in biaxial strain indicating that this effect is related to orientation of the loading axis and not the shape of the grains.

Also, slightly different roughening rates were observed in these experiments for different lots of the same alloy, a common industrial observation. Working with the NIST Center for Neutron Research and the MSEL Ceramics Division, neutron diffraction and X-ray diffraction measurements were used to analyze changes in the crystallographic texture of samples induced by biaxial strain as shown in the pole figures below. From these measurements it was determined that the different initial starting textures of the alloy lots were responsible for the observed difference in roughening rates.

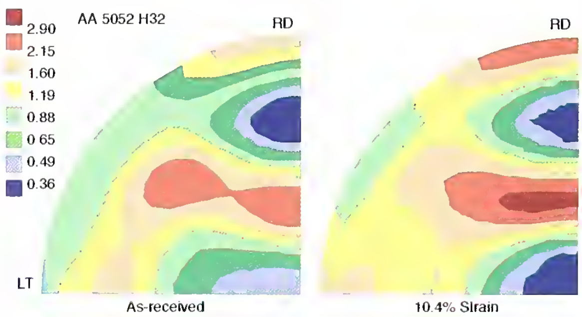



**Figure 2. Influence of biaxial strain on (111) pole figure.**

To enable investigation deformation dynamics in springback, and formability, a high frequency response thermal-mechanical testing machine was acquired. This system will enable NIST to relate fundamental dislocation structures and dynamics to the behavior important to the forming industry.

**Contributors and Collaborators:** D. J. Pitchure, T. J. Foecke, D. Dayan, L. Ives, M. Vaudin, H. Prask, and T. Gnaupel-Herold (NIST/MSEL), and A. Rollet and G. Rohrer (Carnegie Mellon University)

# Fundamental Studies of Plastic Deformation

*A substantial increase in the use of aluminum alloys and high strength steels in automobiles would greatly increase fuel efficiency. A major reason why this has not yet been done is a lack of accurate deformation models for use in designing the stamping dies. An improved understanding of the fundamental processes that are responsible for the mechanical properties would allow the development of such a model. This project is developing a physically based model of plastic deformation using a combination of statistical physics approaches and advanced measurement techniques.*

Lyle E. Levine

Plastic deformation of metals (as in cold rolling, stamping, drawing, extrusion, or metal fatigue) is of great importance to industries worldwide, and improvements in the basic technology would have a significant effect on our economy. As one example, stamped metal parts comprise about a third of the weight of an automobile. If the currently used mild steel could be replaced by aluminum alloys or high strength steels, weight could be reduced considerably, thus greatly increasing fuel economy.

The design of new metal products is often accomplished by computer simulation of the production process using empirically-derived constitutive equations. Unfortunately, existing constitutive equations cannot accurately predict the material behavior, and many tryout and redesign steps are required. For stamped aluminum parts for automobiles, this trial and error process is prohibitively expensive and more accurate constitutive laws are required. We are working on developing constitutive laws that are based upon the underlying physical processes that produce the observed mechanical behaviors.

The fundamental problems involved in this project are formidable. Researchers around the world have been working on this topic for nearly 70 years and, until recently the prospects for success have been poor. In recent years, however, tremendous progress has been made in the areas of statistical physics and experimental techniques. These advances are now being applied to the problem of deformation and progress has been rapid.

NIST is deeply involved in this research activity and coordinates a growing multi-institutional project that currently includes 16 researchers from 2 national labs (NIST and Pacific Northwest National Laboratory) and 3 universities (Washington State University, Massachusetts Institute of Technology and University of Maryland Baltimore County). The project includes work on theory, experiments and computer simulations. Approximately half of this research is conducted at NIST.

The major activities currently underway at NIST include finishing the mathematical development of *strain percolation theory*, a statistical physics theory for how strain propagates through a metal during deformation. Comparison with experimental results was necessary, so a new experimental effort to obtain these data was implemented. This effort has just started using a combination of transmission electron microscopy (TEM) and atomic force microscopy (AFM) to explore the relation between the internal microstructure and the surface slip features. Figure 1 shows an AFM image of the surface of an aluminum single crystal, deformed *in situ*.

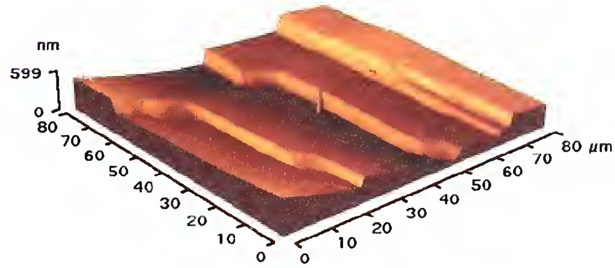



**Figure 1. Slip bands on the surface of an aluminum sample. The sample was deformed to 15 %, polished electro-chemically, and deformed *in situ* in an AFM.**

Each of the large steps is a *slip band*. Higher resolution images show that these bands are composed of many smaller steps called *slip lines*. TEM studies of identical samples clarify the underlying deformation microstructure.

Another topic that theorists at NIST are working on is why the slip lines collect into distinct bands. This heterogeneous nature of slip is important since it occurs at the "boundary" between microscopic and macroscopic deformation. Any physically-based model of macroscopic deformation must include this effect.

Finally, NIST researchers are developing completely new experimental techniques using high-intensity X-ray beams at national synchrotron facilities. Rapid advances have taken place in ultra-small angle x-ray scattering (USAXS) imaging, a revolutionary imaging technique first demonstrated by NIST in 2000. Among these advances are a four-fold increase in spatial resolution and the demonstration of stereo USAXS imaging in which three-dimensional images are acquired.

**Contributors and Collaborators:** D. E. Kramer, D. J. Pitchure, M. F. Savage, R. Thomson , G. G. Long (NIST/MSEL), Y. Shim (University of Georgia), H. Zbib (Washington State University), J. Gan and J. Vetrano (Pacific Northwest National Laboratory)

# Process Models for Particle Reinforced Composites

*The primary objective of this project is to facilitate the introduction of lightweight powder metallurgical materials into automobiles in support of the U.S. auto industry's goal to develop automobiles with substantially higher energy efficiency and lower emissions. This is being accomplished by providing models for lightweight metal consolidation, measurements and data for model validation, software that readily transfers the models, and the data required for implementing the models to the auto companies and their suppliers.*

Richard J. Fields

Major research efforts within the U.S. auto industry are driven by the need to reduce the weight of future vehicles to meet the U. S. Council for Automotive Research (USCAR) and Partnership for a New Generation of Vehicles (PNGV) goals. This can most readily be accomplished by the substitution of lightweight materials for the heavy materials currently used. This project aids the commercial development of a low cost powder processing technology for aluminum alloy and particle reinforced aluminum (PRA) parts. The aim is to substitute aluminum alloy and aluminum composite powder metallurgy (PM) materials for iron-based PM products. This approach has been recognized by the auto industry, and the technical barriers to success have been identified: the cost of existing powder processing routes is too high, and the production of acceptable parts using press-and-sinter and direct powder forging is not yet achieved. NISTis addressing these needs through a focus on modeling each step in these consolidation processes from powder to fully dense part. Modeling provides the basis for knowing what properties and parameters of a powder or a process need to be measured in order to more rapidly design successful processes and to monitor consistency. Physical modeling of the process can be used with a cost model to make decisions that optimize cost and properties. The modeling is complex and has been carried out with significant academic and industrial collaboration. NIST's primary role has been to coordinate the modeling efforts between academia and industry, validate the models, and provide industry with working models and a preliminary data base. In collaboration with MatSys Inc., the modeling is being made available to industry in a user-friendly, commercially supported software package.

The NIST powder consolidation modeling effort has established a validated set of equations that describe the densification of reinforced (or unreinforced) metal powder in terms of the processing conditions. These equations are used in a commercial software package that accurately models potential processes and that saves U.S. industry time and money otherwise spent on trial-and-error investigations.

NIST reports its results quarterly to an industrial consortium consisting of the three U.S. auto producers, Valimet, Stackpole, Saint Gobain, Hoeganaes, and Mascotech. This group was organized by USCAR and tracked by PNGV.

In past years, studies at NIST of the green strength of aluminum powders showed that bonding was by an interlocking mechanism, rather than oxide rupture followed by metal bonding. Strength measurements showed that small additions of SiC resulted in increased green strength due to a particle shape that was conducive to interlocking. However, at higher SiC concentrations the strengthening was compromised by increased SiC to SiC contacts which have virtually no strength. The maximum strengthening effect was found to depend on the ratio of reinforcement particle size to aluminum particle size and concentration of reinforcement. In FY2001, this effect has been modeled successfully using a percolation theory approach (see Figure 1).

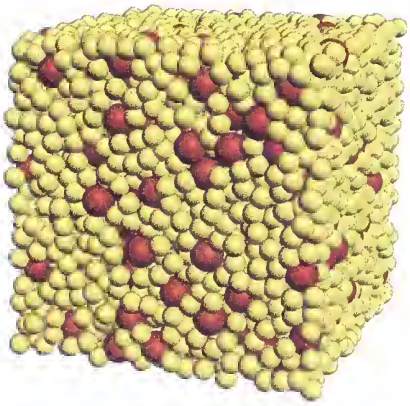


**Figure 1. Percolation model of reinforcing particles (red) in aluminum powder (yellow) matrix.**

Comparison of this model with experimental results was presented at the U.S. Congress on Computational Mechanics in August 2001. While we plan to refine the model of green strength of composite powders, our responsibilities in the U.S. Automotive Materials Partnership (USAMP) project have been fulfilled. We will continue attending quarterly meetings and working with USAMP project members on modeling and materials issues through their final prototyping phase.

**Contributors and Collaborators:** J. Fink, D. E. Harne, L. E. Levine, and Y. Shim (NIST/MSEL), W. Jandeska (GM), R. Chernakov (Ford), G. Lynn (Daimler Chrysler), G. Campbell (Valimet), N. Chawla (University of Arizona), M. F. Ashby and N. Fleck (Cambridge University), I. Anderson (Ames Laboratory), and P. J. Blau (ORNL)

# Materials Data and Metrology for Machining Simulation

*The U.S. spends $200 billion annually on machining of metal parts. Industry studies have shown that considerable improvements in the efficiency of these operations are possible. Also, the rapid development of tooling and high-speed machines makes traditional knowledge-based approaches to improved efficiency ineffective. Predictive modeling has been promoted by industry as a method to realize the improved efficiency. Through this project NIST will provide measurement capabilities and materials data needed to make accurate predictions with these models.*

Richard Fields

Machining of metal parts, e.g. turning, milling, drilling, broaching, etc., to required dimensional tolerances is an essential part of the manufacturing process. Efficient processes can greatly reduce the price of a part and enhance the competitive position of the manufacturer. A recent survey by the Kennametal Corporation found that industry chooses the correct tool for machining a part less than 50% of the time. Advances in machines and tooling stimulated by the NIST Advanced Technology Program (ATP) has made obsolete the traditional, experience-based approaches to finding the optimal process parameters such as feed rate, cutting rate, tool material, tool shape, etc. Pressure from international competitors is driving industry to seek more cost-effective means of choosing process parameters through modeling and simulation. Current models give impressive results, but data to validate these results is nearly nonexistent. This Metallurgy Division project is advancing the state-of-the-art in two areas: (1) fundamental advanced machine metrology, and (2) measurement of fundamental data on the behavior of materials at the high strain and heating rates needed for input into the models. This project within the MSEL Metallurgy Division is part of a larger ATP intramural collaboration with MEL, ITL, and PL. The research in Metallurgy is directed at obtaining the materials data in item (2). This effort requires an extension of our current capabilities in high-rate heating to include high rate straining.

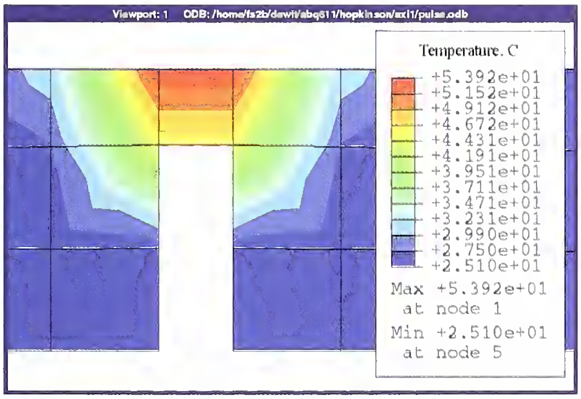



**Figure 1. Temperature distribution due to heat pulse.**

Three significant activities have been completed this year. First, a model of the modified Hopkinson bar compression test device to include high-rate heating has been designed and modeled. This model has permitted us to explore various approaches to obtaining uniform heating of the sample during the test.

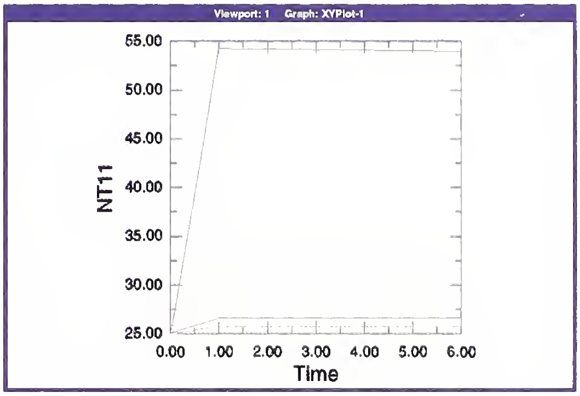



**Figure 2. Temperature transients at points along bar during and after pulse heating.**

Second, a Hopkinson bar compression tester has been constructed that will provide strain rates of the order of $10^5$ per second and heating rates of $10^3$ °C per second. Third, calibrations were completed that assure that the temperatures measured during the high rates of heating are accurate. In the next year, the facility will be used to develop databases on a variety of materials of interest to the machining industry. These data will be used in simulations of prototypical machining operations and compared to the advanced machine metrological database. Evaluation of various models and simulations will provide direction to future research in this area.

**Contributors and Collaborators:**

D. Basak, L. Levine, and R. deWit (NIST/MSEL), M. Davies, R. Rhorer, R. Polvani, K Jurrens, B. Dutterer, and M. Kennedy (NIST/MEL), T. Burns (NIST/ITL), and H. Yoon (NIST/PL)

# Materials for Magnetic Data Storage

For the magnetic data storage industry, the market potential is vast and growing, but global competition is intense, and the technical challenges extreme. Leading commercial magnetic disk drives today store about 25 gigabits of data per square inch. The National Storage Industry Consortium (NSIC) plans to demonstrate a recording density of 1 terabit per square inch—40 times today's level—by 2006.

New materials are needed that have smaller grain structures, can be produced as thin films, and can be deposited uniformly and economically. Recording heads must be designed to produce higher output signals and lower noise. Component dimensions must be made smaller, and the measurements more precise. New lubricants are needed to prevent wear as spacing between the disk and head becomes smaller than the mean free path of air molecules. New methods are needed to standardize components and increase yields.

The National Institute of Standards and Technology is working to achieve these goals. For the past century, NIST has been helping U.S. magnetic data storage industries invent and manufacture product with superior reliability. NIST offers state-of-the-art technology, measurement tools, and standards—many of which cannot be found elsewhere—as well as a reputation for technical excellence and neutrality. Staff expertise spans all fields relevant to magnetic data storage, including materials science, electrical engineering, physics, mathematics and modeling, manufacturing engineering, chemistry, metrology, and computer science. By addressing important measurement issues in magnetism, by bringing together the industrial and scientific communities through the organization of workshops and conferences in the area, and by the development and preparation of appropriate standards, NIST acts to accelerate the use of advanced magnetic data storage materials by the industrial sector, and to enable industry to take advantage of new discoveries and innovations. In addition, close linkage with NSIC increases the industrial relevance of our program and improves technology transfer. Additional collaborations with Xerox, General Motors, Hewlett Packard, IBM, Seagate, and Motorola Corporations, for example, enable NIST to leverage its activities with the much larger, but complementary, capabilities of other organizations.

In FY2001, the Program on Materials for Magnetic Data Storage in the Materials Science and Engineering Laboratory focused on the following projects that were continued from the previous year:

- Processing of magnetic multilayers for optimal giant magnetoresistance effect (Metallurgy Division)
- Magnetic domain imaging and micromagnetic modeling of magnetic domains for understanding magnetization statics and dynamics in recording heads and magnetic media (Metallurgy Division)
- Understanding the nanotribology of magnetic hard disks through the measurement of stiction, friction, and wear at the nanometer scale (Ceramics Division)
- Measuring nanoscale magnetic interactions and structure in multilayers, nanocomposites, and low dimensional systems, needed for understanding and applying materials physics at small scales (Metallurgy Division, NIST Center for Neutron Research)
- Measuring and understanding the origin of magnetic exchange bias in conventional and advanced magnetic structures and devices (Metallurgy Division, NIST Center for Neutron Research)
- Developing a measurement system for magnetic susceptibility of small samples at high frequencies (Metallurgy Division)
- Preparing magnetic measurement standard reference materials. (Metallurgy Division)

Two new projects were initiated in FY2001:

- Processing and measuring the properties of "spintronic" systems wherein spin-dependent magnetic devices are integrated directly onto semiconductor chips (DARPA-sponsored; Metallurgy Division)
- Developing measurements of magnetic damping (NIST Nanotechnology Initiative Funding with EEEL; Metallurgy and Materials Reliability Divisions.)

**Contact Information: Robert D. Shull**

# Materials for Giant Magnetoresistance and Spintronics Applications

*The objective of this program is to provide assistance to U.S. companies manufacturing products based on the giant magnetoresistance (GMR) materials and developing products based on creation and manipulation of spin-polarized electrons. Our work in GMR provides U.S. companies with significant competitive help by investigating the science underlying the manufacturing process of these nanometer scale devices. In the area of Spintronics, we are examining fundamental materials issues in the identification and fabrication of magnetic materials whose electrons exhibit 100% spin polarization.*

William F. Egelhoff, Jr.

Computer memory and hard-disk-drive products are a major force in today's economy, representing over $50B in annual sales, worldwide. The current generation of hard-disk drives read stored bits using ultrathin films which exhibit the giant magnetoresistance (GMR) effect. In order to maintain exponential growth rates in storage density ever larger values of the GMR effect are required. In addition to hard-disk applications, emerging markets for GMR include nonvolatile memory chips, magnetic field sensors, and ultrahigh speed isolators. For the last five years, our research has focused on GMR materials, particularly on surfactants that improve interface flatness during growth and thereby increase specular scattering and on the effect of layer thickness and pinholes on magnetic coupling. A growing research area is in the identification and fabrication of magnetic materials whose electrons exhibit 100% spin polarization for imaging and spin electronics (Spintronics) applications.

**GMR Thin Films.** The idea of surfactant-assisted growth of metal films was pioneered at NIST in the 1980's and is now widely used in industry. This year introducing one monolayer of Ag as a surfactant early in the growth process was found to increase GMR of Co/Cu/Co films through a smaller magnetic coupling between Co layers, especially in spin valves with very thin Cu layers. Transmission electron microscopy suggests that Ag helps to suppress pinholes in the Cu. Although Ag is not as successful in improving spin valve properties as oxygen, the most successful surfactant we have found so far, these data contribute to our understanding of the role of both surfactants and pinholes in determining GMR.

Pinholes in ultrathin films are the largest impediment to achieving increased magnetoresistance values in GMR spin valves and magnetic tunnel junctions. We have developed a novel method of studying pinholes. We deposit a sandwich structure, such as Co/$Al_2O_3$/Co, in which the film to be investigated for pinholes has a magnetic thin film above it and one below it. One magnetic film is pinned magnetically in a fixed direction, while the other is free to switch in an applied field. If pinholes are present, the free film is partially pinned by the contact with the pinned film. By studying the magnitude of this "transfer of pinning" through pinholes, we can determine, directly, the influence of pinholes. The novel aspect of this work is that we separate the influence of pinholes from the influence of magnetostatic "orange peel" coupling by measuring the "transfer of pinning" at cryogenic temperatures. The influence of pinholes has a strong temperature dependence while magnetostatic "orange peel" coupling is temperature independent. We are using this novel approach to improve our understanding of the thin-film growth processes that lead to pinholes. This understanding may lead to better methods for suppressing pinholes.

**Spin-Polarized Electrons.** In collaboration with the Naval Research Labs we have developed growth techniques to deposit magnetic tunnel junctions on GaAs substrates. The structure of the junctions is typically Fe/$Al_2O_3$/GaAs. The electron tunneling properties through an insulator like $Al_2O_3$ are a sensitive function of deposition and processing conditions. These conditions were optimized, and the shape of the intensity-voltage curves indicate that our structures can be used to inject electrons from Fe ballistically into GaAs. This property is important since ohmic contacts do not inject spin-polarized electrons into semiconductors. Ballistic injection appears to be the best hope for achieving this key goal of Spintronics. Our next step will be to deposit these structures on 2-D quantum-well structures incorporated in GaAs to look for circularly polarized photon emission, which is the definitive proof of spin injection. This work is supported by DARPA.

For Spintronics and magnetic imaging, magnetic materials are needed whose electrons exhibit 100% spin polarization. In a DARPA-sponsored study we have demonstrated that $CrO_2$ can be grown on H-terminated Si(100), $Al_2O_3$/H-terminated Si(100), polycrystalline $\alpha$-$Fe_2O_3$, polycrystalline NiO, thermal oxide on Si(100), Ta, Ti, and Al films oxidized by exposure to air, and on STM probes of Al, PtIr, Co, Ti, Au, Cr, and W, as well as $TiO_2$ and $Al_2O_3$ single crystal substrates. A collaboration with the University of Maryland is investigating magnetic imaging with these coated STM probes.

**Contributors and Collaborators:** R. D. McMichael (NIST/MSEL), M. Stiles ( NIST/PL), 6 U.S. Corporations, 2 Federal Laboratories, 7 U.S. Universities, 8 International Universities

# Magnetization Control in Thin Magnetic Films

*For many applications of magnetic thin films in devices, it is important to be able to control the magnetization direction of a thin film in a way that is insensitive to elevated temperatures. We are providing measurement methods, computational methods, and data on the thermal stability, magnetization control and micromagnetics of thin magnetic films to the magnetic recording, magnetic sensor, and other magneto-electronic industries.*

Robert D. McMichael

This project is concerned with the thermal stability of "spin valve" multi-layer films, the micromagnetics of magnetization control in thin films, and dynamic measurements of thin magnetic films. In FY2001, we are wrapping up our work on robust magnetization control methods, allowing us to shift our attention to new efforts in magnetization dynamics and damping.

The magnetization in a thin magnetic film must be held fixed in a certain direction or "pinned" for proper operation of read heads in disk drives. In earlier generations of read heads, pinning was accomplished by coupling one of the Co layers to an antiferromagnetic "exchange biasing" material.

More recently, however, the trend among head manufacturers has been toward substituting a Co/Ru/Co synthetic antiferromagnet (SAF) trilayer for one of the Co films. The Ru layer creates a strong coupling between the adjacent Co layers that tends to align the magnetizations antiparallel. In this configuration, the net interaction with an external field is much weaker than for a single Co film, so the SAF trilayer is harder to switch.

While the SAF structure has a decreased interaction with an applied field, it still requires stabilization because 1) the net moment of the SAF is not exactly zero, and 2) the SAF is unstable to a spin-flop transition in which the magnetizations in the Co layers rotate nearly perpendicular to the applied field, and slightly toward the applied field. The SAF is typically stabilized using an antiferromagnetic exchange bias material.

Previously, we had found that a large anisotropy can be produced in Co films by using an obliquely deposited underlayer of Ta. The oblique deposition creates an anisotropically rough surface which is filled in by the Co. Anisotropy fields in excess of 0.1 T (1 kOe) can be generated by as little as 5 nm of Ta (see Figure 1). These results were published in 2000.

In FY 2001, we have found that the anisotropy arising from the oblique Ta underlayer can be used to pin the SAF structure very effectively. Switching fields in the SAF were as high as 0.15 T (1.5 kOe) when the bottom Co layer of the SAF was made 0.5 nm to 0.7 nm thicker than the upper layer (see Figure 2). This extra thickness was needed to balance the SAF structure by compensating for the a magnetically "dead" layer at the Co/Ta interface.

This demonstration shows that obliquely sputtered Ta can provide stable pinning of the SAF structure without using thicker, thermally unstable, often corrosion prone antiferromagnetic materials, possibly resulting in more stable, reliable magnetic sensors and disk drives. Preparation of a final publication on these results is underway.

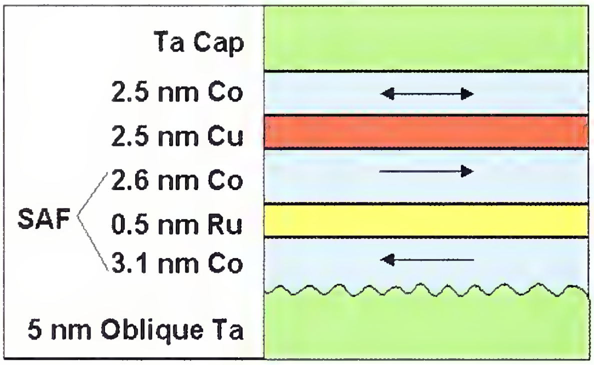



**Figure 1. Schematic structure of a spin valve with an oblique Ta underlayer to stabilize the Co/Ru/Co SAF trilayer.**

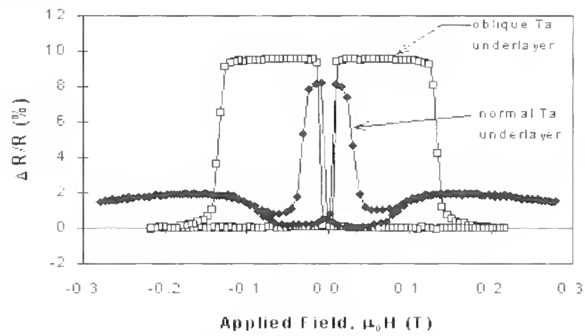



**Figure 2. Magnetoresistance curves for two SAF-pinned spin valves deposited on oblique Ta and normally sputtered Ta underlayers. The obliquely deposited Ta underlayer stabilizes the SAF structure. The spin flop transition is visible as a bump in the normal Ta spin valve curve starting at 0.06 T.**

## Contributors and Collaborators:

J. Bonevich, R. Fry, and D. Mathews (NIST/ MSEL); C.-G. Lee (Changwon National University, Korea), and Y.-W. Tahk (KAIST, Taejon, Korea)

# Nanomagnetodynamics

*The objectives of this MSEL-EEEL collaboration are to provide industry with (1) an improved understanding of magnetic damping mechanisms, (2) improved magnetic damping measurements and standards, and (3) data on methods for controlling magnetic damping in technically relevant materials. The knowledge, measurement methods, standards and data generated by this project will enable industries involved in magnetic information storage to predict and control magnetization on shorter time scales and in smaller dimensions, enabling faster and smaller magnetic data storage devices.*

Robert D. McMichael

This new project funded under the National Nanotechnology Inititative is focusing on magnetization damping mechanisms and measurement of damping and damping control in thin magnetic films. In FY2001 we constructed a new broadband ferromagnetic resonance spectrometer, performed calculations of defect-induced phonon generation and measured linewidth in films with intentional defects. In collaboration with EEEL, our future plans include studies of switching dynamics with controlled damping. Damping time is important for high data rate reading and writing in disk drives and in magnetic memory (MRAM) chips under development. The magnetization-lattice coupling that governs damping is also important for the stability of written bits in the ultra high density disk drives of the near future. One of the best ways to measure damping is by ferromagnetic resonance, where the width of the peak in susceptibility at the precession frequency includes the effects of damping. Unfortunately, the width of the susceptibility peak, or "linewidth," also includes the effects of inhomogeneities and defects in the material. A straightforward (but incorrect) assessment of the effect of inhomogeneity on the linewidth would equate the linewidth to the dispersion in the local precession frequency in the material. Our measurements show in a dramatic fashion that the "two-magnon" model gives a much more accurate description of extrinsic linewidth. The two-magnon process scatters the uniform precession into degenerate spinwaves, and is not a form of true damping since the energy does not transfer to the lattice, but stays in the magnetization. In addition to two magnon broadening, defects can couple the magnetization to sound waves. We calculated the magnetic damping rate due to generation of sound waves and found that this effect was several orders of magnitude too small to describe the measurements of damping in thin films, meaning that the two-magnon process does not mask a significant amount of true damping to the lattice.

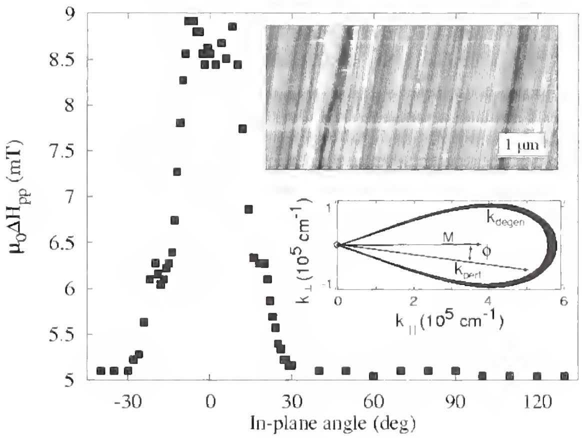



**Figure 1. Ferromagnetic resonance linewidth in a 64 nm film of $Ni_{80}Fe_{20}$ as a function of magnetization direction relative to parallel scratches in the substrate (top inset). M is perpendicular to the scratches at 0°. The scratches contribute to linewidth only when perturbation wavevectors coincide with wavevectors of degenerate spinwave modes (bottom inset).**

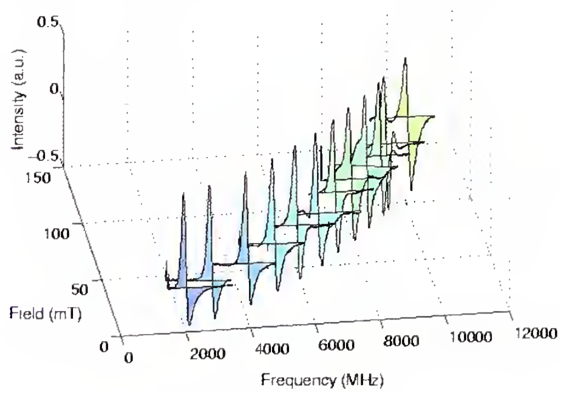



**Figure 2. Ferromagnetic resonance signals from a 50 nm thick film of $Ni_{80}Fe_{20}$ measured on a new broadband spectrometer constructed this year. The instrument is capable of measurements up to 20 GHz. The frequency dependence of ferromagnetic resonance linewidth is especially important for discriminating between different damping mechanisms.**

## Contributors and Collaborators:

D. J. Twisselmann, A. B. Kunz, J. E. Bonevich D. E. Mathews, W. F. Egelhoff, Jr., A. P. J. Chen , D. C. Hurley (NIST/MSEL), and S. E. Russek , T. J. Silva, and J. M. Moreland (NIST/EEEL)

# Magnetic Properties of Nanostructured Materials

Robert D. Shull and Richard A. Fry

*In the past 10 to 15 years there has been a remarkable improvement in the technology for materials preparation resulting in today's capability of controlling morphology and features at the nanometer level. In magnetism, such control allows the fabrication of nm-thick (or separated) composite materials of dissimilar magnetism, leading to materials with novel bulk magnetic character and unusual property combinations. In order for U.S. industry to take advantage of these new materials, their behavior needs to be understood and their method of proper measurement determined. We are providing materials metrology to do that.*

Since the recognition of nanomaterials' potential in science and technology, NIST has been a major advocate for a U.S. Government R&D focus on nanotechnology. Robert Shull and Michael Cassasa served on the interagency committee that developed the National Initiative on Nanotechnology. Robert Shull will continue to work with NSF, ONR, AFOSR, NIH, DOE, and NASA on establishing national priorities through FY2002. In addition, Dr. Shull is a leader in the international nanoscience and nanotechnology community.

The nanomaterials project in the Metallurgy Division has focused on developing an understanding of the magnetic behavior of nanoparticles as a function of size, composition, and interparticle spacing. The current areas of research are in dendrimers containing magnetic particles and nano-ferrofluids.These two areas were chosen because they not only are simple systems for which the particles sizes and spacings can be controlled, but also have possible industrial applications.

**Magnetic dendrimers.** For the first time ever, NIST, in collaboration with the University of Michigan, have created magnetic dendrimer nanocomposites by forming Fe, Co, and Ni nanoparticles (0.3 % mass fraction) in hydrophobic polyamidoamine (PAMAM) dendrimer hosts and then embedding them in a polystyrene matrix.This technique facilitates the formation of ferromagnetic clusters of well-defined size and spacing, and puts them in a solid form easily measured at low temperatures and high magnetic fields. SQUID magnetometry on these nano-composites showed that after subtraction of diamagnetic polymer background, at 300 K all exhibited paramagnetic behavior with magnetization (M) being linear with applied magnetic field (H). Curie-Weiss (1/M vs. T) graphs supported this conclusion by displaying a linear high temperature behavior with only small deviations below 100 K.

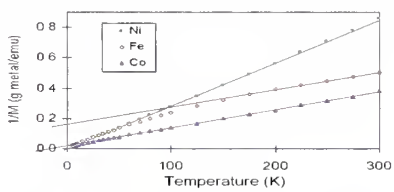



**Figure 1. (1/M) vs T for Ni, Fe-, and Co-containing dendrimers exhibiting straight line fits at high temperatures (Curie-Weiss behavior) with small deviations at low temperatures, particularly in the case of Fe.**

**Nano-ferrofluids.** To probe particle interaction effects two different suspensions of Fe-oxide were studied. Figure 2 shows data measured for (40 to 80) nm diameter maghemite ($\gamma$– $Fe_2O_3$) suspensions in a carboxylic acid. Differences between field cooling (FC) and zero field cooling (ZFC) were observed for all materials, but the magnetic strength did not simply scale with the dilution (i.e., particle size) as expected, indicating unusual particle interaction effects. Despite the interactions, the nanometer size maghemite led to superparamagnetism in all samples.

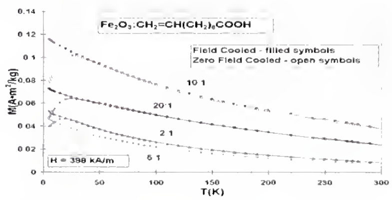



**Figure 2. Magnetization behavior as a function of temperature for $\gamma$-$Fe_2O_3$ suspensions in carboxylic acid, with concentrations as labeled.**

In contrast, 7 nm diameter colloidal $Fe_3O_4$ particles suspended in alkylnaphthalene behaved differently. For these materials, their superparamagnetic M vs. H behavior observed at 300 K for different concentrations superimposed when appropriately scaled by the dilution (i.e., interparticle separation), indicating the lack of magnetic interactions. Since particle size and separation are usually equivalent variables, differences in magnetic behavior of the two "nano-ferrofluids" highlights the need for improved characterization and modeling.

**Nanocomposite refrigerants.** In a project partially supported by NASA, successful preparation of magnetic nanocomposite refrigerants from Fe-containing dysprosium-gallium garnets was accomplished in FY2001. The powders show superparamagnetic behavior and enhanced magnetocaloric effects of magnitudes similar to those found earlier in Gd-Ga-Fe magnetic nano-composite garnets. These results extend NIST's invention of nanocomposite magnetic refrigerants with enhanced magnetocaloric effects.

**Contributors and Collaborators:** C. Silva (Federal University of Pernambuco), S. Taketomi (Matsumoto, Inc.), A. Uhlman (NewYork Polytechnic Institute), L. Balogh (University of Michigan), and B. Bauer, V. Provenzano, and J. Li (NIST/MSEL)

# Magneto-Optical Indicator Film (MOIF) Technique

Alexander J. Shapiro, Robert D. Shull

*Understanding of the magnetization reversal mechanism in a material is fundamental to understanding the magnetic character of that material. For coupled magnetic systems, in particular, detailed knowledge of their magnetization reversal processes holds the key to enabling their commercialization. Developed by NIST and ISSP RAS, the advanced magneto-optical indicator film (MOIF) imaging technique provides a unique method for studying such processes. Our goals are (1) to develop MOIF into a widely available and broadly useful technique for dynamic imaging and (2) to use it to perform leading-edge research in magnetic dynamics.*

The MOIF technique is a quantitative, simple, fast, illustrative, and sensitive tool for nondestructively characterizing materials' magnetic microstructures at the micron scale and the real-time visualization of the elemental events of the magnetization process. A transparent YIG film with in-plane anisotropy is placed on top of the sample. Polarized light passing through the indicator film is reflected by a thin Al underlayer and the normal component of the magnetic stray field from the sample (e.g., as would exist at a domain wall or sample edge) is detected by its effect in locally magnetizing the yttrium iron garnet (YIG) film out of plane. Consequently, it is possible to determine the location of domain walls and magnetization directions in the vicinity of crystal edges and defects by contrasts in the polarization rotation of reflected light from the indicator film due to the double magneto-optic Faraday effect.

The quality of the magneto-optical imaging is greatly enhanced by digital image processing: magnetic imperfections of the indicator film and inhomogeneities in the illumination are practically eliminated, image contrast is strongly increased, and quantification of the magnetic information becomes possible.

We have recently applied the MOIF technique for studying the magnetization reversal process in thin nanocomposite magnetic multilayer systems, in which technologically important effects, such as unidirectional anisotropy, and exchange hardening, which enhances the maximum energy product, have been observed. One such system we investigated this year was a synthetic antiferromagnet (SAF) proposed for use in the technologically important sensors based on the giant magnetoresistance (GMR) effect. Specifically, we investigated the magnetization reversal mechanism in the SAF structure Co/Ru(0.5 nm)/Co stabilized by a large (0.1 T) magnitude, uniaxial anisotropy (in excess of 120 kA/m) induced by an obliquely sputtered Ta underlayer.

The obliquely deposited Ta layer and both Co layers varied in thickness, and the main result of this study was a finding that the reversal mechanism was accomplished by domain wall nucleation and growth, rather than by rotation of the magnetic moments (as was previously observed in the SAF deposited on an antiferromagnet). A canted magnetization state is formed between the two ferromagnetic (Co) layers which has often been attributed to biquadratic coupling between ferromagnetic layers. Here, we have found that a canted spin structure can also be formed by competition between antiparallel coupling (across the Ru layer) and ferromagnetic coupling (via pinholes through the Ru).

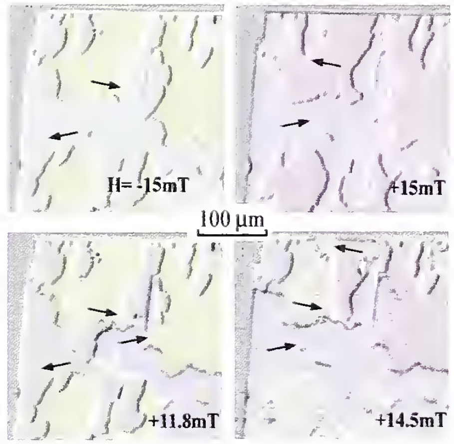



**Figure 1. MOIF Images of the SAF structures Co/Ru(0.5 nm)/Co stabilized by uniaxial anisotropy.**

Knowing the magnetization reversal mechanism is critical to the understanding of that material's behavior and its subsequent application. Since very thin layers of any material will possess pinholes, the present discovery will certainly have an impact on the future development of advanced thin film magnetic materials (e.g., for permanent magnets, transformers, sensors). The MOIF technique will also become an indispensible analytic tool.

**Contributors and Collaborators:** R. D. McMichael and W. F. Egelhoff (NIST/MSEL), V. I. Nikitenko (Johns Hopkins University), and V. S. Gornakov (ISSP, Russian Academy of Sciences)

# Magnetic Properties and Standard Reference Materials

*Users of magnetic materials, including the recording industry, the permanent magnet industry, and the manufacturers of electric motors and transformers of all types, need standard reference materials (SRM's) to calibrate instruments used to measure the critical magnetic properties of their starting materials. The Magnetic Materials group is developing such a suite of standards. Methods for improving the efficiency and accuracy of measuring and characterizing magnetic materials of industrial importance are also under investigation.*

Robert D. Shull and Robert D. McMichael

Commercial instruments for the measurement of magnetic properties are relative instruments that rely on known samples for their calibration. To produce standard samples for such instruments, an absolute magnetometer was developed and assembled at NIST. A picture of this instrument is shown below. Modifications to the absolute magnetometer to improve its sensitivity have been made during the current reporting period. These improvements have enabled the development of standards with much smaller magnetic moments.

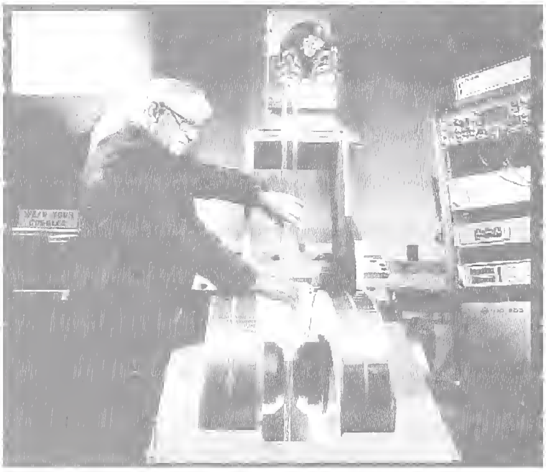


**Figure 1. NIST absolute magnetometer.**

Prior to FY2001, two SRM's had been issued: a nickel sphere (SRM 772a) and a nickel disc (SRM 762). As a result of the improved sensitivity of the NIST magnetometer, two new SRMs were under development this year. The first was a 1 mm diameter yttrium iron garnet (YIG) sphere for use in calibrating the more sensitive ranges of magnetometers. In addition, it will be useful for calibrating very sensitive instruments such as alternating gradient magnetometers and SQUID magnetometers. Because of its high resistivity, the YIG sphere should also be useful for calibrating the magnitude and phase in alternating current magnetometers. The second SRM is a platinum cylinder paramagnetic susceptibility standard. This will be useful in calibrating the zero field point and linearity of magnetometers because of its absolutely linear magnetization vs. magnetic field relationship resulting from its paramagnetic nature. In addition, it will also be useful for calibrating the field scale after the magnetization scale has been calibrated. Pd, Al, and $MnF_2$ susceptibility SRMs are planned for the future.

In addition to the improved sensitivity, the automated measurement capability of the absolute magnetometer shown at left has been improved, as has the temperature measurement system. The temperature dependence of the Ni and YIG spheres and the Ni disk were determined. This information will make these SRMs, currently certified only near room temperature, more useful in the many commercial magnetometers which measure over extended temperature ranges. The Ni disc SRM has also been selected this year as the sample material to be used by the members of the International Disk Drive Equipment and Materials Association (IDEMA) for the round robin measurement of magnetic strength.

A thin film magnetic moment standard is being assessed jointly with the Magnetics Technology Division of the Electronics and Electrical Engineering Laboratory. Thin Ni films (3mm x 4mm x 2nm) lithographically prepared inside a planar superconducting coil have been examined metallurgically for homogeneity in thickness, coverage, and adhesion, and measured magnetically to determine their magnetic moment. Several films have been observed, and a thin film SRM for calibrating B-H loopers appears feasible for FY2002.

This past year, NIST helped organize the Third International Symposium on Hysteresis and Micromagnetics Modeling in Ashburn, Virginia which addressed recent theories, measurements, and other developments in hysteresis, with the primary focus on magnetics. Of the 65 attendees from 16 foreign countries almost all the leading experts in micromagnetic computation were present. The attendees felt that the symposium provided an unusually productive occasion for them to present and exchange ideas, methods and results. Included in that discussion were several anecdotes on how the NIST Standard Problems in Computational Micromagnetics had caused the international community to re-evaluate and improve its computational codes. The proceedings from the symposium will be published in Physica B.

**Contributors and Collaborators:** L. J. Swartzendruber, R. A. Fry, A. J. Shapiro, R.V. Drew, D. E. Mathews, G. E. Hicho, L.C. Smith, and F. S. Biancaniello (NIST/MSEL), D. Pappas and F. DiSilva (NIST/EEEL), Industrial and Academic Collaborators, and L. H. Bennett and E. Della Torre (George Washington University)

# Materials for Microelectronics

Today's U.S. microelectronics and supporting infrastructure industries are in fierce international competition to design and produce new smaller, lighter, faster, more functional, and more reliable electronics products more quickly and economically than ever before.

Recognizing this trend, in 1994 the NIST Materials Science and Engineering Laboratory (MSEL) began working very closely with the U.S. semiconductor, component and packaging, and assembly industries. These early efforts led to the development of an interdivisional MSEL program committed to addressing industry's most pressing materials measurement and standards issues central to the development and utilization of advanced materials and material processes within new product technologies, as outlined within leading industry roadmaps. The vision that accompanies this program – to be the key resource within the Federal Government for materials metrology development for commercial microelectronics manufacturing – may be realized through the following objectives:

- Develop and deliver standard measurements and data;
- Develop and apply *in situ* measurements on materials and material assemblies having micrometer- and submicrometer-scale dimensions;
- Quantify and document the divergence of material properties from their bulk values as dimensions are reduced and interfaces contribute strongly to properties;
- Develop models of small, complex structures to substitute for or provide guidance for experimental measurement techniques; and
- Develop fundamental understanding of materials needed in future microelectronics.

With these objectives in mind, the program presently consists of twenty separate projects that examine and inform industry on key materials-related issues, such as: electrical, thermal, microstructural, and mechanical characteristics of polymer, ceramic, and metal thin films; solders, solderability and solder joint design; photoresists, interfaces, adhesion and structural behavior; electrodeposition, electromigration and stress voiding; and the characterization of next generation interlevel and gate dielectrics. These projects are conducted in concert with partners from industrial consortia, individual companies, academia, and other government agencies. The program is strongly coupled with other microelectronics programs within government and industry, including the National Semiconductor Metrology Program (NSMP) at NIST.

FY2001 Projects (and division leading project)

**Lithography/Front End Processing**

- Characterization of Ultrathin Dielectric Films (Ceramics)
- Lithographic Polymers (Polymers)

**On-chip Interconnects**

- Interconnect Materials and Reliability Metrology (Materials Reliability)
- Measurements and Modeling of Electrodeposited Interconnects (Metallurgy)
- Thin Film Metrology for Low K Dielectrics (Polymers)

**Packaging and Assembly**

- Packaging Reliability (Materials Reliability)
- Solder Interconnect Design (Metallurgy)
- Solders and Solderability Measurements for Microelectronics (Metallurgy)
- Tin Whisker Mechanisms (Metallurgy)
- Wafer Level Underfill Experiment and Modeling (Metallurgy)
- Wire Bonding to Cu/Low-K Semiconductor Devices (Metallurgy)
- X-ray Studies of Electronic Matls. (Materials Reliability)

**Crosscutting Measurements**

- Dielectric Constant and Loss in Thin Films and Composites (Polymers)
- Electron Beam Moiré (Materials Reliability)
- Ferroelectric Domain Stability Measurements (Ceramics)
- Measurement of In-Plane Thermal Expansion and Modulus of Polymer Thin Films (Polymers)
- Mechanical Properties of Thin Films (Ceramics)
- Permittivity of Polymer Films in the Microwave Range (Polymers)
- Polymer Thin Films and Interfaces (Polymers)
- Texture Measurements in Thin Film Electronic Materials (Ceramics)
- Thermal Conductivity of Microelectronic Structures (Materials Reliability)

**Contact Information: Frank W. Gayle**

# Solder and Solderability Measurements for Microelectronics

Frank W. Gayle, William J. Boettinger, Carol A. Handwerker, Ursula R. Kattner, and Maureen E. Williams

*Solders and solderability are increasingly tenuous links in the assembly of microelectronics as a consequence of ever shrinking chip and package dimensions and the movement toward environmentally friendly lead-free solders. We are providing the microelectronics industry with measurement tools and data to address solder issues. A thermodynamic database has been publicly distributed for modeling lead-free solder systems. We also work closely with industry groups on measurement tools needed for development of lead-free solders for use in harsh environments, and provide guidance for adoption of these solders into assembly processes through work with industrial standards organizations.*

The U.S. microelectronics industry has clearly articulated the measurement needs for Pb-free solders and for solderability and assembly. For example, the urgency for materials data for Pb-free solders has been specified in the 1997 IPC, 1999 International Technology Roadmap for Semiconductors, 2000 National Electronics Manufacturing Initiative (NEMI), and 2000 IPC Lead-Free Solder Roadmaps. The pressure from the Japanese consumer product market and from the European Union to produce lead-free microelectronics continues to increase. In addition, the lack of understanding and control of current standard solderability measurements has inhibited the development of improved measurements necessary for new solders and for new packaging schemes. These industrial needs are addressed under this NIST project.

NIST has taken a major role working with industry through a NEMI Task Force to identify and move Pb-free solders into practice. NIST co-chairs the NEMI Alloy Group which is responsible for providing key measurements and data needed to understand manufacturing and reliability issues. This year, NIST held a workshop cosponsored by NEMI, the National Science Foundation, and The Metallurgical Society on Modeling and Data Needs for Lead-Free Solders. The report from this workshop is serving as a roadmap for research on the reliability of lead-free solders. In addition, NIST is currently evaluating the metallurgy and thermal cycle performance of boards assembled by NEMI to evaluate Pb-free solder performance with a variety of components, with and without Pb contamination (see figure).

NIST was also active in the National Center for Manufacturing Sciences (NCMS) High Temperature Fatigue Resistant Solder Consortium, including 8 companies in the microelectronics and automotive industries, which completed a four-year project this year to develop Pb-free solders for harsh environment applications, such as automotive and telecommunications. NIST lead the alloy selection task group and took the lead in writing the final report. NIST accomplishments and future directions are described above in the Highlights section.

In a third major activity, NIST has developed a database needed to calculate multicomponent phase diagrams essential for Pb-free alloy development. This phase diagram project is described under "Thermodynamic Databases for Industrial Processes."

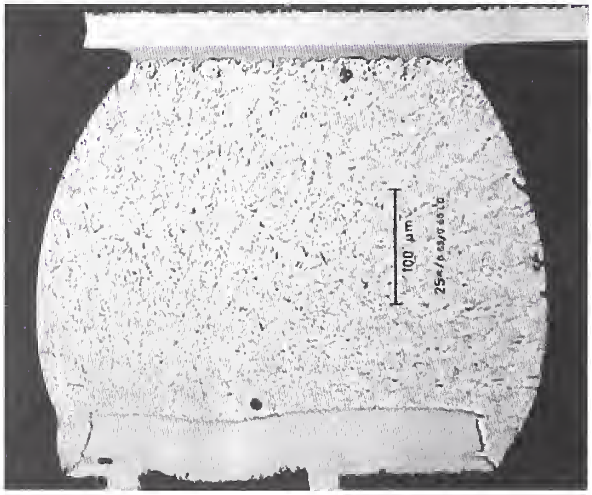



**Figure 1. Metallographic cross-section of a lead-free SnAgCu solder selected under the NIST-led NEMI Pb-free Alloy Task Group. The chip-scale package shown here has been assembled with a SnPb component finish to determine how Pb contamination affects reliability.**

We are also working in collaboration with IPC Standards Committees (most closely with members from Celestica, Lucent, Raytheon, Rockwell, and Shipley-Ronel) to establish reproducible solderability test standards for board assembly. Activities include providing benchmark experiments for the wetting balance tests to predict on-line solderability for a wide range of surface finishes, lead materials, and solder alloys. New NIST research to develop electrochemical solderability tests and an understanding of whisker formation in Sn-based, Pb-free electroplated surface finishes complements the solderability studies.

Highlights from our work include:

- Sources of uncertainty have been established for wetting balance solderability tests, leading to increased repeatability and reproducibility of tests.
- Recent flux studies performed at NIST have led to a change in test procedures for the IPC/EIA J-STD ANSI solderability standards.

**Contributors and Collaborators:** L. C. Smith (NIST/MSEL), K-W. Moon (University of Maryland), D. Napp (National Center for Manufacturing Sciences, and associated consortium members), and R. Gedney (NEMI Lead-Free Task Force, and associated consortium members)

# Assembly of IC Chips Utilizing Wafer-Level Underfill

*Assembly of advanced area array microelectronic chips and components requires self-alignment of interconnects with restoring forces supplied by molten solder joints. To provide the necessary detailed understanding of the restoring forces provided by misaligned solder joints, we are providing computer simulations as well as experimental studies that verify the accuracy of these simulations. As a result, we demonstrate that the restoring force to be expected during assembly of flip chips with an underfill/solder bump system applied at the wafer level can be accurately predicted using such codes as the public-domain Surface Evolver software.*

Daniel Josell and Daniel Wheeler

This project involves experimental studies and computer modeling of the geometries of solder joints subjected to a range of loading conditions. The ability of capillary (surface energy) based models to predict solder joint restoring forces has been determined. The relationship between restoring force and solder joint misalignment obtained in this work determines the restoring forces responsible for flip-chip realignment during reflow operations. Wafer-level underfill, which is deposited prior to solder joint formation, retards self-alignment of the chip and substrate promoted by the molten solder joints. Underfill between a chip and substrate reduces solder joint fatigue; wafer-level underfill eliminates the need for time-consuming infiltration after chip attachment. A model that incorporates the solder joint restoring force relationship and the viscous drag associated with the wafer-level underfill has been developed.

The capillary realignment forces for different pad dimensions and solder volumes were experimentally measured. Solder joints with volumes of eutectic lead-tin solder down to 0.0023 mm$^3$ were studied with pad diameters down to 0.35 mm. The loading conditions were systematically varied and the post-solidification solder joint geometry measured in order to obtain the force-displacement relationships for the solder joints under both aligned and misaligned conditions. The experimental results were compared to predictions of our model which is based on the commonly used Surface Evolver freeware computer code. This model considers only capillary and gravitational forces to predict solder joint geometries.

The predictions of the model were shown to be consistent with the results of the experiments. As a result, this class of computer codes has been shown to be an accurate means of studying solder joint restoring forces for wafer-level underfill applications. This model has been extended to combine the restoring force information obtained in the first part of this study with viscosity data for wafer-level underfill materials. A range of realignment behaviors is predicted, with key parameters being the mass of the flip-chip, the restoring force relationship and number of solder joints, the equilibrium standoff-height and the viscosity of the underfill material.

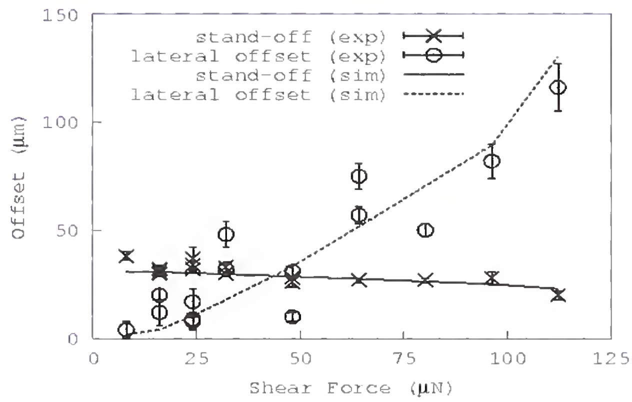



**Figure 1. Measured lateral offset (misalignment) and normal offset (standoff height) for ≈0.0023 mm$^3$ $Pb_{63}Sn_{37}$ solder connecting 0.35 mm diameter pads as functions of applied shear force. The curves are predictions of Surface Evolver.**

Realignment can occur through monotonic decrease of the misalignment or through oscillation about the equilibrium location, with all of the noted parameters affecting the particular behavior.

An article to appear in the Journal of Electronic Packaging presents the results of this study. In addition, the software developed in this project has been made publicly available on the Center for Theoretical and Computational Materials Science CTCMS web site:

http://www.ctcms.nist.gov/~wd15/solder/

as part of the library of Evolver files modeling different industrial solder joint geometries. The generality of the joint geometries that can be studied using this code is a significant benefit.

**Contributors and Collaborators:** W. Wallace and C. Schultheisz (NIST/MSEL)

# Evaluation of Bond Pads for Wire Bonding

*Several problems that are encountered in wire bonding to advanced damascene copper/low-K devices result from 1) oxidation of the copper pads during handling, wafer sawing, and high temperatures encountered during die attachment and thermosonic bonding, and 2) diffusion of copper into the top surface metal/inhibitor coating. NIST is evaluating the direct deposition of gold onto damascene copper as a top coat oxidation inhibitor while determining the diffusion coefficient of electrodeposited copper into gold for bondability impact.*

Christian E. Johnson and David R. Kelley

The introduction of copper and low dielectric constant (LoK) polymers into advanced ultra-large scale integration (ULSI) copper-damascene chips have created new wire bonding challenges. Three areas of particular interest are: 1) oxidation inhibitors to ensure bondability to the top surface, 2) low modulus, low dielectric constant materials positioned underneath the pad, and 3) under-pad mechanical support structures. There are also various polymer/metallurgical interactions (resulting in long term device reliability problems) that can occur as the result of the wire bonding process over low modulus, LoK, materials with barriers. These include cracked diffusion barriers, copper diffusion into the LoK polymers, spalling/crazing of the polymers, and bond pad indentation (cupping).

In the past, bonds have been made to aluminum pads over silicon or oxide. This presented an ideal metallurgy and a rigid platform for thermosonic bonding. However, with the introduction of LoK alternatives, copper pads may be positioned over low modulus polymers that are themselves encased in brittle barriers. This can lead to bond yield and/or reliability problems.

Although there are a number of areas that must be considered in wire bonding to advanced Cu/LoK devices, this project focuses on the top surface metal that is present to promote bondability. Specifically, we are evaluating gold coatings placed directly on copper as an oxidation inhibitor and determining the impact that interdiffusion of copper and gold may have on long term reliability for wire bonding. Gold- copper bond interfaces have been shown by Lucent Technologies to be more reliable than Au-Al interfaces which are currently used approximately $10^{12}$ times/year in devices today.

Gold has traditionally been the top metal surface of choice on Cu for wire bondability, usually with a Ni barrier between it and the Cu. However, the Ni is an extra manufacturing step and can diffuse through the gold (by grain boundary diffusion) and result in unbondable nickel oxide on the surface. Fortunately, gold can be directly plated onto Cu. When gold and copper interdiffuse, they primarily form superlattice structures, which are ductile and not considered a reliability hazard. Cu will diffuse through Au and oxidize on the surface; however, it diffuses more slowly than Ni through Au. The diffusion coefficient of the copper (damascene-process) into and through an autocatalytic Au film has not been established. Solution additives, such as a few ppm of Pb to slow down grain boundary diffusion, inhibit autocatalytic deposition. Thus, in order to avoid copper diffusing to the Au surface during the various packaging thermal steps, the Au thickness should be greater than 0.5 mm. Measurements are currently being made of the diffusion coefficient on a first-time-of-arrival Auger hot-plate technique so that a more accurate (minimum) thickness can be determined.

A constraint in using Au (or any other plated metal) on a chip is that the Au must be plated by a non-electrolytic process, since some of the semiconductor pads may have no ground-return connection. To achieve this in our work, a two-step immersion/autocatalytic deposition process had to be adopted, since the available autocatalytic gold would not deposit directly onto Cu. The copper surface was first primed with an immersion gold that resulted in a 10 nm primer coating. This step was followed by a pH-neutral autocatalytic gold build-up to the (0.5 to 1) mm desired thickness. Ball bonding tests were conducted on these films to establish adhesion and bondability. The films were then deposited on silicon test chips having bond pads of approximately 0.5 mm of damascene-process copper. Bondability was established with manual ball bonders using both 60 and 120 kHz ultrasonic frequencies. The bonding stage was maintained at 150 °C. Shear test results established that the bonds made at both frequencies were approximately 80% welded. Although the long term reliability of the Au/Cu interface (bonded or plated) is known, data from damascene-Cu structures is still needed. This will be the focus of future work.

**Contributors and Collaborators:** G. G. Harman (NIST/EEEL), E. Steel (NIST/CSTL), C. Evans (NIST/MEL), D. Frear, T-A. Tran, and L. Yong (Motorola), and R. Augur (International Sematech)

# Measurements for Electrodeposited On-Chip Copper Interconnects

Daniel Josell and Thomas P. Moffat

*Copper has rapidly been introduced into chip interconnection technology as a replacement for aluminum. Electrodeposition is the preferred deposition method due to its unique ability to superconformally fill high aspect ratio features when organic inhibitors and accelerators are added to the plating bath. NIST has recently developed a predictive capability for the influence of additives on superconformal deposition. This capability is based on the development of an electrochemical signature for superfill, a quantitative model for interface motion and competitive adsorption, and the demonstration of deposition down to 75 nm trench widths.*

The mechanism responsible for superconformal electrodeposition of copper in high aspect ratio features has been determined. Simulations from a model based on this mechanism have been shown to predict results of electrodeposition filling experiments in trenches as small as 90 nm wide and 450 nm deep. No fitting parameters are required to model this behavior.

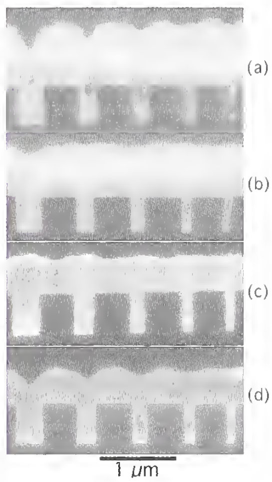
These developments have built upon two recent Metallurgy Division discoveries. First, a simple electrolyte was developed that yields superconformal electrodeposition of copper in trenches as small as 75 nm wide. Second, hysteresis in cyclic current-voltage studies of copper deposition on flat copper specimens in an electrolyte was found to be indicative of the ability of that electrolyte to yield superconformal deposition in fine features. Those results demonstrated that superconformal deposition only occurs when both an inhibiting additive and an accelerating additive are present in the electrolyte.

For the model, we obtain kinetic parameters for particular electrolytes from cyclic voltammetry experiments described above. These kinetic parameters describe both the rate at which the dilute accelerating additive accumulates on the copper surface, displacing the inhibiting additive that retards local copper deposition, and the impact this accumulation has on the local copper deposition rate.

The new model uses these parameters to predict filling of features. The most important and novel aspect of this model is its recognition of the fact that local coverage of accelerator changes both by accumulation from the electrolyte and by changes of the local area upon which it has accumulated. *Accumulation of accelerator at the bottom of superfilling trenches is dominated by the latter, geometrical effect.* The decreasing area of the copper surface growing up from the bottom of fine features thus results in increasing accelerator coverage on this surface. This, in turn, accelerates copper deposition there, resulting in filling of the trench from the bottom upward, i.e., superconformal deposition. The finer the feature, the more important area change *can* be – it requires an appropriately designed electrolyte composition and appropriate deposition conditions to take full advantage of this effect.

Experimental fill results are compared with model predictions in Figures 1 and 2, respectively. Note the agreement of fill versus failure to fill. Also note the overfill bumps – the model shows that this so-called "momentum plating" is due to the enhanced accelerator coverage on the upward moving surface. These results also explain the initial period of conformal plating (uniform deposition on all surfaces) visible through the model as the time required for significant accumulation of accelerator from the electrolyte.

This model provides a means of rapidly assessing electrolytes for superfilling submicron features on the basis of the rapid, inexpensive cyclic voltammetry studies on flat copper. Only those electrolytes that yield filling according to the model predictions need be moved to full scale testing of fine feature filling. We are now working with Texas Instruments to intergrate NIST models and measurements in TI production.



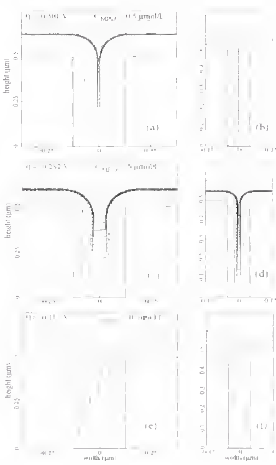



**Figure 1 (left) Superfill results for accelerator concentrations of (0, 0.5, 5 and 40) mMol/L (top to bottom). A window for superfill exists around the 5 mMol/L concentration.**

**Figure 2 (right) Model predictions for the second largest and smallest trenches for accelerator concentrations of (0.5, 5 and 40) mMol/L. Vertical seams indicate failure to fill.**

**Contributors and Collaborators:** D. Wheeler and J. E. Bonevich (NIST/MSEL)

# Mechanism of Sn Whisker Growth from Electrodeposits

*The electrodeposition of metallic alloys has been central to the growth of the electronics industry. This is largely due to the exceptional properties exhibited by electrodeposited material as well as the favorable economy of scale associated with electrodeposition processes. A technology important to electronics manufacturing is the electrodeposition of Sn-based coatings and surface finishes to guarantee solderability. With the rapid move to Pb-free solder surface finishes, new test methods are needed for predicting the tendency of such coatings to form Sn whiskers that can lead to catastrophic failures.*

Christian E. Johnson, Maureen E. Williams, and Kil-Won Moon

The National Electronics Manufacturing Initiative (NEMI) Pb-Free Task Force, of which NIST is a member, has identified a serious concern of original equipment manufacturers (OEMs), contract manufacturers, and component manufacturers with the conversion from Sn-Pb to Pb-free surface finishes for circuit boards and component leads. It is well known that the use of pure Sn protective surface finishes can cause serious problems: tin whiskers (1 μm diameter and several mm long) can grow from the plated tin surface and cause electrical shorts and failure. Historically Pb was added to Sn plate to prevent whisker growth, and thus the "whisker problem" disappeared. With the rapid move to environmentally-friendly Pb-free assemblies, the microelectronics industry must remove Pb from the surface finishes. For many applications an electroplated Sn-based surface finish remains a preferred surface for ease of processing, however the possible growth of whiskers is currently a perilous drawback.

Based on these needs, this NIST project is focusing on: (1) understanding the effect of alloying elements other than Pb on the tendency for whisker formation; (2) developing techniques to separate possible physical and microstructural factors affecting whisker formation, and (3) assisting the NEMI Standardization Technology Integration Group (TIG) with both test development and understanding the root causes of whisker formation. The Sn-Cu system was chosen as the most versatile for electroplating, since it is compatible with Sn-3.9Ag-0.6Cu and Sn-0.7Cu, the Pb-free solders selected as the new national standard alloys by NEMI for reflow soldering and for wave soldering, respectively.

Whiskers are generally believed to grow to relieve residual stress in electroplated Sn. However the origin of this stress has yet to be determined definitively. In the process of studying the mechanisms for whisker growth, we have developed methods to control grain size, residual stress and alloy composition in order to sort out underlying factors in whisker growth. The probability of whisker growth from as-deposited Sn electrodeposits has been measured as a function of copper ($Cu^{2+}$) additions to a commercial bright water-based methanesulfonate electrolyte. To provide reproducible plating conditions and to approximate flow conditions in commercial strip plating, a rotating disk electrode assembly was used.

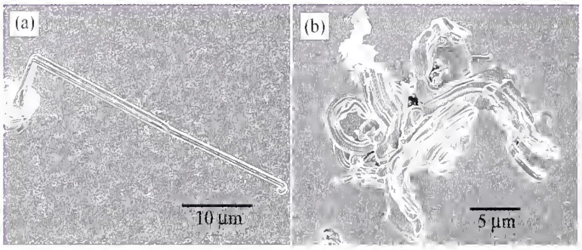



**Figure 1. Defects include both (a) whiskers and (b) eruptions.**

A fixed plating current at 25 °C was used to produce deposits 3 μm and 10 μm thick. Two substrates were used: free standing 250 μm thick pyrophosphate Cu deposits and 40 nm thick fine grain Cu evaporated onto a Si (100) wafer. Electrolyte $Cu^{2+}$ concentrations from 0 to 25 x $10^{-3}$ mol/L produced deposits with average Cu compositions between 0 % and 3.3 % mass fraction, respectively.

As shown in Figure 1, both whiskers and eruptions appear as defects. In the absence of Cu additions, no defects were observed on either substrate after 60 days of room temperature aging. With Cu additions, no whiskers were observed on the Cu-coated Si substrates, but whiskers were observed within two days on the free-standing Cu substrates increasing to a density of $10^2$/mm$^2$ for the highest Cu contents as indicated in the Table. The deposits on the free-standing Cu and Cu evaporated onto Si (100) substrates had different preferred orientations, (103) and (101), respectively, but the effect of Cu on the deposit microstructure was the same. The increase in Cu content reduced the grain size of the Sn deposit from 0.65 μm to 0.2 μm, independent of substrate. Much of the Cu in the deposits occurred as Cu-rich particles on the Sn grain boundaries. The primary correlation observed was that Sn-Cu deposits with (103) preferred orientation were most likely to form whiskers.

We continue to be active participants in the NEMI TIG where test methods are being developed and where experimental results are shared. Our goal is to provide an understanding of the fundamentals of the whisker formation, which ensures that the test developed by the NEMI group will have widespread applicability.

**Contributors and Collaborators:** W. J. Boettinger and G. R. Stafford (NIST/MSEL)

# Metals Characterization

Engineering design depends on the specification of the properties of the materials that are used. Equally important, manufacturers and their suppliers need to agree on how these properties should be measured. The MSEL Metals Characterization Program, centered within the Metallurgy and the Materials Reliability Divisions, spans the measurement spectrum from the innovative use of state-of-the-art measurement systems, to leadership in the development of standardized test procedures and traceability protocols, to the development and certification of Standard Reference Materials (SRMs).

The NIST effort in metals characterization has a strong emphasis on electron microscopy, which is capable of revealing microstructures within modern nanoscale materials and atomic-resolution imaging and compositional mapping of complex crystal phases with novel electronic properties. The MSEL microscopy facility consists of two high-resolution transmission electron microscopes (TEM) and a high-resolution field-emission scanning electron microscope (FE-SEM) capable of resolving features down to 1.5 nm. Novel experimental techniques using these instruments have been developed to study the mechanical properties of multilayered and nano-scaled materials.

The Metals Characterization Program is contributing to the development of test method standards through committee leadership roles in standards development organizations such as ASTM and ISO. In many cases, industry also depends on measurements that can be traced to NIST Standard Reference Materials (SRMs). This program generates the following SRMs for several quite different types of measurements.

Hardness of Metallic Materials (Metallurgy Division): Hardness is the primary test measurement used to determine and specify the mechanical properties of metal products. The hardness standardization project is providing industry with primary transfer standards for the Rockwell hardness and Vickers and Knoop microhardness scales. These SRM test block standards are used for the periodic calibration of hardness testing machines.

Magnetic Properties (Metallurgy Division): The need for reliable magnetic measurements is becoming increasingly acute because of new technologies involving magnetic phenomena in data storage and microelectronics. Such measurements require calibration of magnetometers using certified magnetic standards in several different shapes and magnetic strengths, and with a wide range in magnetic character. These standards are now being produced under this program.

Coating Thickness (Metallurgy Division): Coating thickness standards are produced by electrodeposition and are widely used for calibration of coating-thickness measuring instruments. SRM coupons are produced with a wide range of thicknesses, and are bar coded to allow analysis of degradation and life expectancy when the standards are returned for verification.

Charpy Impact (Materials Reliability Division): The Charpy impact machine verification project provides rapid, accurate assessment of test data generated by our customers using SRM Charpy standards, and, where merited, certifies the conformance of Charpy impact test machines to ASTM Standard E 23. Participation in ISO Committee TC 164, assures that specimens and procedures are compatible with international standards.

In addition to the SRM activities above, NIST (Materials Reliability Division) provides assistance to the Bureau of Reclamation (BOR) on metallurgical issues that arise during maintenance, inspection, and failure assessment of dams and water conveyance infrastructure projects. NIST advice and data provide BOR engineers with an independent check of other input.

**Contact Information: Samuel R. Low, III**

# Mechanical Properties of Multilayered and Nanomaterials

Tim Foecke, Donald Kramer, Dan Josell

*Mechanical performance of layered structures is critically important to large sectors of industry: reliability of microelectronic devices, tribology of magnetic media, and integrity of advanced aerospace thin film coatings. Predictive design of mechanical properties relies heavily on knowledge about how these materials deform and fracture at very fine scales. Research in this project is aimed at determining what deformation mechanisms operate in these classes of materials as a function of layer thickness and constituent materials using novel experimental techniques. This information will be useful in designing devices and modeling layered systems.*

Nanomaterials have been found to exhibit a number of extraordinary mechanical properties. Strengths and hardnesses that are many times that of either constituent material have been observed in nanograined (3D) and nanolayered (1D) structures. In particular, multilayered materials with wavelengths in the micron and submicron regime offer exciting opportunities, because the ability to fabricate these materials using physical vapor deposition (PVD) or electrodeposition makes these economically viable to produce. Also, one can use pairings of materials that are immisible, and not able to be conventionally processed.

Recent *in situ* TEM observations of cracking in Cu/Ni nanolaminates have revealed a possible explanation for the extreme flaw sensitivity of this class of materials. As seen in the Figure 1, cracking progresses behind an extremely localized plastic zone. While there is negligible plasticity away from the crack, within the crack zone, plastic strains in excess of 30 % are seen. This correlates well with *ex situ* fracture observations of thin foils, where no plasticity is measured but high ductility is observed on the fracture surface. The structure studied appears to lack a mechanism for work-hardening, leading to extremely easy localization. The results from our mechanical property measurements are being used by theory groups at Ohio State and Los Alamos National Lab to modify their models of these structures. These groups are now concentrating on the details of how dislocations interact with interfaces, and how interfaces act as barriers to dislocation motion.

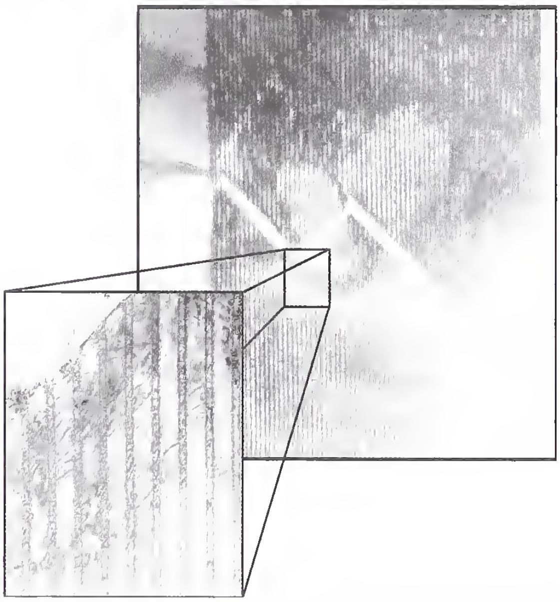


**Figure 1. TEM micrograph of crack in 30 nm Cu / 60 nm Ni single crystal nanolaminate. Note extension of plasticity upon deflection of crack path.**

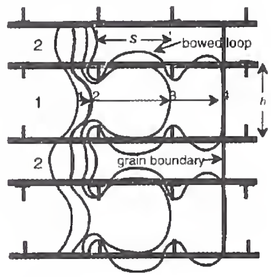



**Figure 2. Schematic of model detailing progression of "Orowan" dislocation bows through the structure in TEM micrograph (from Peter Anderson, OSU).**

Another facet of the project deals with the high-temperature structural stability and mechanical behavior of Nb / $Nb_5Si_3$ microlaminated materials. Work performed in conjunction with researchers at Johns Hopkins University has determined how to form these structures so that they are stable for hundreds of hours at temperatures exceeding 1300 °C.

The Air Force is interested in this class of materials for use as a strong, damage tolerant critical coating on jet engine turbine blades, and is investigating whether microlaminated silicide / refractory metal microlaminates may be used to form hollow turbine blades in the absence of any superalloy substrate.

**Contributors and Collaborators:**

T. Moffat, D. Smith and G. White (NIST/MSEL), T. Weihs and D. van Heerden (Johns Hopkins University), P. Anderson (Ohio State University), H. Kung, J. Hirth, and R. Hoagland (LANL), and J. Embury (McMaster)

# Hardness Standardization: Rockwell, Vickers, and Knoop

*U.S. industry needs to be able to make measurements that are traceable to national standards and compatible with the measurements made in other countries. This need is being emphasized by the requirements of quality standards such as ISO 17025. For the measurement of hardness, NIST is meeting this need by standardizing U.S. national hardness scales, producing hardness reference standards, and providing assistance and guidance to U.S. industry through national and international standards activities.*

Sam R. Low, Christian E. Johnson, James L. Fink, and David R. Kelley

Hardness is the primary test measurement used to determine and specify the mechanical properties of metal products. The Metallurgy Division is engaged in all levels of standards activities to assist U.S. industry in making hardness measurements compatible with other countries around the world. These activities include the standardization of the national hardness scales, development of primary reference transfer standards, leadership in national and international standards writing organizations, and interactions and comparisons with U.S. laboratories and the National Metrology Institutes of other countries.

**INTERNATIONAL ACTIVITIES:** At the international level, we are participating in the Working Group on Hardness (WGH) under the International Committee for Weights and Measures (CIPM). The primary goal is to standardize hardness worldwide. As secretary of the WGH, we participated in an international Key Comparison of Vickers hardness scales, and prepared the U.S. Hardness Calibration and Measurement Capability data for the international Mutual Recognition Arrangement (MRA). We also head the U.S. delegation to the ISO committee on hardness testing of metals, which oversees the ISO hardness test method standards.

**NATIONAL ACTIVITIES:** Our primary task at the national level is to standardize the U.S. national hardness scales and to provide a means of transferring these scale values to industry. Currently, we are producing test block Standard Reference Materials® (SRMs) for the Rockwell, Vickers and Knoop hardness scales, as well as developing new reference standards. Eight different microhardness SRMs for Vickers and Knoop hardness are currently available. Using electro-deposition technology, the standards are produced with uniform properties and microstructure. This year, a mechanical polishing procedure for copper was developed, substantially improving the number of standards that can be produced. We also completed the development and began calibration of three new SRMs for the Rockwell B scale (HRB) to complement the three SRM Rockwell C scale blocks currently available. The HRB scale is used for testing softer metals, such as aluminum, copper and brass. These new HRB standards should be available for sale in early 2002.

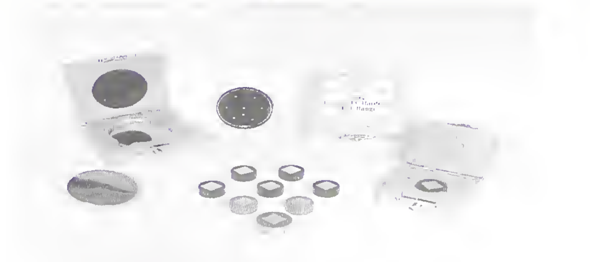
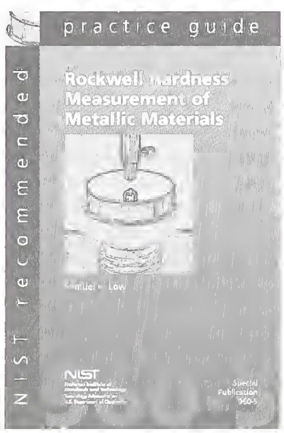


**Figure 1. SRM test blocks for Rockwell hardness and Vickers and Knoop microhardness**

In addition to developing SRMs, our national standards activities include chairing the ASTM hardness subcommittee E28.06. To assist ASTM, the Metallurgy Division, with the assistance of the NIST Information Technology Laboratory, drafted a new procedure for determining the uncertainty of Rockwell hardness measurements, currently being balloted for approval as a new appendix to the Rockwell hardness test method standard ASTM E18. This procedure was requested by manufacturing companies and hardness calibration agencies that have recently begun determining hardness measurement uncertainties as required by accreditation programs.




In May, the Metallurgy Division published a new NIST Recommend Practice Guide: Rockwell Hardness Measurement Of Metallic Materials. The Guide helps to explain the causes of variability in Rockwell hardness test results and supplements the information given in test method standards with good practice recommendations. Since it has become available to the public, over 3000 copies have been requested, including some hardness equipment manufacturers that will be providing a copy of the Guide with their products. The Guide is also available for download at http://www.metallurgy.nist.gov/publications.html .

**Contributors and Collaborators:** J. Song, C. Evans, and R. Clary (NIST/MSEL), W. Liggett, Jr. and N. Zhang (NIST/ITL) C. Beauchamp, N. Trahey, D. Faison, and W. Stiefel (NIST/TS), and G. Hicho (NIST/MSEL)

# Electrodeposited Coating Thickness Standards

Standard Reference Materials (SRMs) of nonmagnetic coatings over magnetic substrates, with nominal thickness values ranging from 6.0 mm ( ≈ 0.2 mils) to 2000 mm ( ≈ 80 mils), are produced for use by the organic and inorganic coating industries for nondestructive measurements of coating thickness. Traceability to NIST coating thickness SRMs is specified for a wide range of industrial and military products. Prototype zinc standards for the electrogalvanizing industry are being developed that provide standardization of composition and microstructure.

Carlos R. Beauchamp, Hilary B. Gates, and David R. Kelley

The Electrochemical Processing Group is responsible for producing seventeen different thickness standards of nonmagnetic coatings over magnetic substrates, with thicknesses ranging from 6.0 mm (≈ 0.2 mils) to 2000 mm (≈ 80 mils). Each standard consists of a 1270 mm (≈ 50 mils) thick magnetic steel substrate, electroplated with fine-grain copper of varying thickness, and a thin nonmagnetic layer of chromium for wear resistance. These standards are packaged into preconfigured sets of four coupons. Each set consists of different ranges, depending on the needs of our customers. The standards are certified with a maximum expanded uncertainty of 2 % of the mean at the 95 % level of confidence and are used for the calibration of instruments based on the magnetic pull-off technique or those based on magnetic induction.

These standards are used by the organic and inorganic coating industry for non-destructive measurements of non-magnetic coatings over magnetic substrates. Some of the industries using our standards are paint, electronics, aerospace, automotive, steel, nuclear, railroad, welding, and tool and dye. Typical applications where our SRMs provide a critical need include the evaluation of wear in coatings and coating thickness measurement during the surface finishing stages or the repair of worn parts. In addition, these coating thickness standards are used to verify compliance with minimum coating thickness requirements for corrosion protection as well as thickness tolerances for the successful assembly of coated parts. These standards are also used by coatings industries where properties such as solderability and electrical and thermal conductivity are optimized by the thickness of the coating.

In FY2001, our goal was to deliver the 817 outstanding units for FY2000 and to replenish the inventory of SRMs 1361b and 1364b with 77 additional units. At this time, all 3,576 outstanding coupons have been measured. From these coupons, 646 of the combined 894 units owed have been assembled and the remaining 248 units are in the final stages of labeling and packaging for delivery to NIST's Standard Reference Materials Program.

In addition to our SRM fabrication/certification activities, we are initiating two outreach efforts. The first is the publication of a NIST Recommended Practice Guide which we expect to be available in FY2002. The Practice Guide will focus on the magnetic induction measurement and the uncertainties associated with its application to thin film analysis. In addition to the Practice Guide, we are planning to host a gathering of instrument manufacturers, standards producers, and end-users to discuss their materials and metrology needs for the future. This meeting is expected to take place in Winter 2002. Two new SRMs are currently being developed for the electrogalvanizing industry. The first is a 3 cm x 3 cm zinc-coated steel coupon intended for the verification of gravimetric procedures used in the "weigh-strip-weigh" method for zinc determination. A second standard, used for on-line x-ray fluorescence measurements, is also being developed. Although these coupons will be certified by mass, the industry has requested that the crystallographic texture of the zinc electrodeposit match that produced commercially. Towards this end, we are determining the influence of deposition potential on the crystallographic orientation of electrodeposited zinc from sulfate-based electrolytes.

| SRM | Coating Thickness Values | | | |
|---|---|---|---|---|
| 1358b | 20 μm (0.8 mils) | 80 μm (3.1 mils) | 255 μm (9.8 mils) | 1000 μm (39 mils) |
| 1359b | 48 μm (2.0 mils) | 140 μm (5.5 mils) | 505 μm (20 mils) | 800 μm (32 mils) |
| 1361b | 6 μm (0.2 mils) | 12 μm (0.5 mils) | 25 μm (1.0 mils) | 48 μm (2.0 mils) |
| 1362b | 40 μm (1.6 mils) | 80 μm (3.1 mils) | 140 μm (5.5 mils) | 205 μm (7.9 mils) |
| 1363b | 255 μm (9.8 mils) | 385 μm (16 mils) | 505 μm (20 mils) | 635 μm (26 mils) |
| 1364b | 800 μm (32 mils) | 1000 μm (39 mils) | 1525 μm (59 mils) | 1935 μm (79 mils) |

**Figure 1. Coating Thickness Standard Reference Materials available sets and their corresponding nominal thickness.**

**Contributors and Collaborators:** S. D. Leigh (NIST/ITL)

# Nanoscale Characterization: Electron Microscopy

*Electron microscopy is used to characterize the structure and chemistry of materials at the nanometer scale to better understand and improve their properties. New measurement techniques in electron microscopy are being developed and applied to materials science research. The MSEL Electron Microscopy Facility primarily serves the Metallurgy, Ceramics, and Polymers Divisions but is made available to other NIST staff as well as for outside collaborative research efforts.*

John E. Bonevich

Atomic-scale structure and compositional characterization of materials can lend crucial insights to the control of their properties. For instance, direct observation of local structures by transmission electron microscopy provides an important information feedback to the optimization of crystal growth and processing techniques. Various characteristics may be observed such as crystal structure and orientation, grain size and morphology, defects, stacking faults, twins and grain boundaries, and second phase particles, with details of structure, composition, and internal defects, compositional variations and the atomic structure of surfaces and interfaces.

The MSEL Electron Microscopy Facility consists of two transmission electron microscopes (TEM), three scanning electron microscopes (SEM), a specimen preparation laboratory, and an image analysis/computational laboratory. The state-of-the-art JEOL3010 UHR-TEM has atomic scale resolution as well as detectors for analytical characterization of thin foil specimens. An X-ray detector (EDS) provides compositional analysis and an energy selecting imaging filter (IF) allows compositional mapping at atomic resolution.

Highlights from the EM Facility for FY2001 include:

- A new field-emission SEM (FE-SEM) has been deployed with spatial resolutions of 1.5 nm at 15 kV and 2.5 nm at 1 kV. The FE-SEM allows nano-scale imaging of uncoated specimens, an important consideration for ceramic and polymeric materials.
- A new electron back-scattered diffraction (EBSD) system has been deployed with interfaces to both a conventional SEM and the new FE-SEM. This system allows for detailed, automated texture measurement and, when coupled with EDS, phase identification of unknown materials.
- New linewidth standard reference materials for the semiconductor electronics industry have been characterized. The reference features are based on {111} planes of Si on bonded and etched-back silicon on insulator wafers. Atomic resolution lattice counting provides an absolute measurement of width traceable to the meter (see Figure 1).
- TEM characterization of sub-100 nm electrodeposited copper lines complemented focused ion beam imaging of patterned cross-sections (see Figure 2).

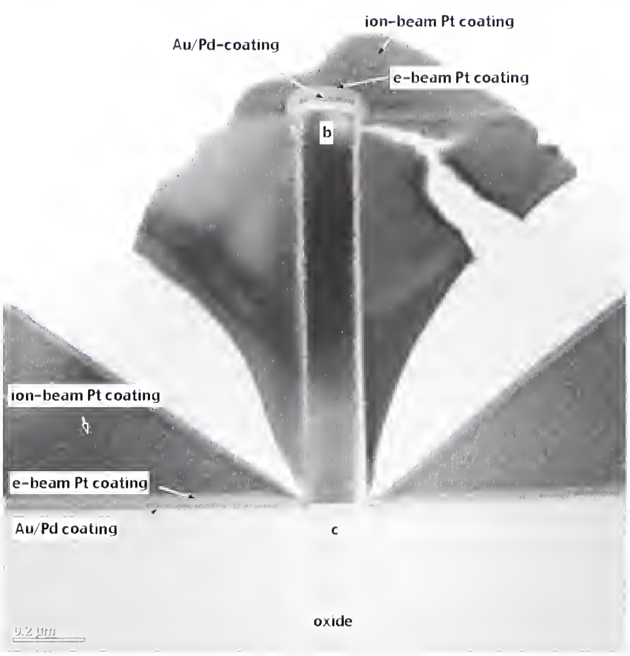



**Figure 1. Cross-sectional TEM view of silicon linewidth feature. The absolute width of the feature can be directly related to the meter.**

**Figure 2. TEM image of copper electrodeposited nanoscale features in "superfilled" trenches. The electrodeposited copper contained microstructural defects such as voids, dislocations and twins that could not be revealed in the focused ion beam imaging.**

## Contributors and Collaborators:

R. D. McMichael, D. Josell, and T. P. Moffat (NIST/MSEL), M.W. Cresswell and R.A. Allen (NIST/EEEL), E. B. Steel and J. H. Scott (NIST/CSTL), and A. Stanishevsky (University of Maryland, Institute for Plasma Research)

# Metals Processing

The Metals Processing Program applies NIST expertise in a wide range of disciplines, including thermodynamics, electrochemistry, fluid mechanics, diffusion, x-ray, and thermal analysis, to understand the processing steps which will lead to products having the desired form and properties, at an acceptable cost. Working with industries ranging as widely as automotive, aerospace, coating, and microelectronics, several important processing problems are being addressed including melting and solidification of welds, castings of single crystals, powder production and consolidation, and coating production by thermal spray and electrodeposition.

The increasingly competitive manufacturing environment fuels the search for new metal alloys as well as efficient processing techniques to fully realize their potential. The processing cycle can include many steps, including a formation process such as casting or electrodeposition, a heat treatment process, a deformation process such as rolling or stamping, joining by welding, or coating to enhance surface properties. In each of these processes, the distribution of crystal phases, the grain structure, the alloy compositional segregation, and the defect structure are altered, with resulting changes in properties such as strength, ductility, corrosion resistance, and conductivity which form the basic rationale for the use of metals in industrial products. The following projects in the Metals Processing Program focus on measurements and predictive models needed by industry to design improved processing methods, provide better process control, develop improved alloy and coating properties, and reduce costs.

- Modeling of Solidification and Microstructure Development: (Metallurgy Division): Models of alloy solidification, crystal growth processes and heat treatment are being developed to aid industry in designing production systems that increase product yield and performance.
- Processing-Structure-Property Data For Thermal Spray Coatings (Metallurgy Division): Coating reproducibility and reliability are addressed by the development and calibration of advanced sensors, applying these measurement tools to the control and characterization of TS coatings, and working with the Thermal Spray (TS) community to establish a coating processing-microstructure-property database.
- Weld Process Sensing, Modeling and Control (Materials Reliability Division): Advanced instrumentation and data analysis techniques are used to develop a better understanding of the underlying physics governing the arc welding process.
- High-energy X-ray Diffraction Studies (Materials Reliability Division): Investigations are underway on the use of high-energy x-ray diffraction as an alternate, nondestructive option to the conventional destructive methods for measuring physical properties.
- Tailored Metallic Powders (Metallurgy Division): Measurement techniques for the characterization of microengineered powders are developed to advance our understanding of the relationships among properties, processing, and microstructure.
- Electrodeposition of Aluminum Alloys (Metallurgy Division): Guidelines for the electrodeposition of aluminum-based alloys from low-temperature, low-vapor pressure non-aqueous electrolytes are being developed as an inexpensive method for producing homogeneous and fine-grained aluminum-based thin films for corrosion protection.
- Electrochemical Processing of Nanostructural Materials (Metallurgy Division): Electrochemical methods for the synthesis and characterization of nanoscale magnetoresistive device architectures are being examined with an emphasis on the use of surfactants and segregation phenomena in controlling homo- and hetero-epitaxial film growth.
- Reaction Path Analysis in Multicomponent Systems (Metallurgy Division): Costly experimental investigations of bonding and reaction processes involving interdiffusion at interfaces between metals, oxides, and vapors are supplanted by models, based on thermodynamic data, that predict the formation of transient phases and rates of reaction in complex multicomponent systems.

Metals Processing projects with an especially strong focus on areas which are of special interest to MSEL have evolved to become part of other program areas such as Materials for Microelectronics and Forming of Lightweight Materials. Because processing plays such a basic role in determining the properties and performance of metals, we expect this program to continue providing a foundation for advanced metals technologies.

**Contact Information: Stephen D. Ridder**

# Modeling Solidification, Electrodeposition and Microstructure Evolution

*Many properties of structural and functional materials depend on the distribution of composition, phases and grain orientations on the scale of 1 to100 nm. The scale of such structures is a natural result of the fabrication processes used in their production, a scale of interface motion which is modeled well by the so-called "phase field" approach. The ultimate goal of this project is to provide a set of phase field modeling tools to simulate the development of complex structures. These models are already providing information to aid industry in designing production systems that increase product yield and performance.*

James A. Warren, William J. Boettinger, Jonathan E. Guyer, and Daniel J. Lewis

Modeling of microstructures produced by solidification, electrodeposition and other processes involves mathematical solution of equations for heat flow, fluid flow, current flow and/or solute diffusion. Boundary conditions on external surfaces reflect the macroscopic processing conditions. Boundary conditions at internal interfaces correspond to the liquid-crystal (grain) or grain-grain interfaces. These internal interfaces are moving boundaries and require boundary conditions with thermodynamic and kinetic character. For solid-solid transformations, stress and strain replace fluid flow as a consideration.

In order to deal with the complex interfacial shapes which develop during solidification, electroplating and grain growth, the phase field method has become the technique of choice for computational materials scientists. This approach often requires numerical techniques to solve the model equations but readily deals with complex interface shapes and topology changes. The research, conducted in the Metallurgy Division, is also supported by the NIST Center for Theoretical and Computational Materials Science (CTCMS).

Dendritic and eutectic growth, generally present in castings, involves extremely complex interface shapes. Several of the accomplishments of this year deal with the application of diffuse interface modeling to these types of growth:

- The phase field approach has been used to describe the growth and final impingement of differently oriented dendritic alloy grains. A previously developed NIST model has been simplified with no apparent sacrifice in accuracy. The new model employs only one more order parameter than standard phase field models of solidification.
- A multiphase field model has also been explored to obtain knowledge about the last stages of solidification. Such information has practical applications in predicting porosity and hot tearing of castings. The temperature required for the bridging (coalescence) of dendritic microstructures has been determined. For comparison, a sharp interface model of this phenomenon has also been developed.
- The effects of vacancies have been included in a phase field model of grain microstructure evolution in order to treat sintering.
- A phase field model of ternary eutectic alloys has been developed and validated in the 2-D binary case by comparing with the classical (Jackson-Hunt) model. Future work will include the microstructure of ternary alloy structures, which requires 3-D modeling.
- Adaptive grid methods are being applied to phase field problems. These numerical techniques allow researchers to automatically numerically resolve the interfacial region of a calculation, improving the speed and accuracy of a calculation. These methods are particularly important for calculations done in three dimensions or where fluid flow is included. A variety of adaptive codes have been collected and are being distributed on the world wide web, through the CTCMS.
- Recent interest in Cu metallization by electrodeposition into small features for integrated circuits has indicated the need for a modeling approach that avoids the simplifications usually employed. Thus, the phase field technique has been applied to electrochemistry. With a single set of governing equations, current is carried by valence electrons in the metal and by ionic diffusion and electromigration in the electrolyte. This model naturally produces the charged double layer at the metal-electrolyte interface. Investigations are underway to determine the phase field kinetic description necessary to recover classical Butler-Volmer electrodeposition behavior.

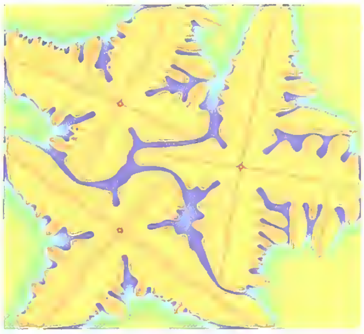


**Figure 1. View of a phase field simulation of 4 alloy dendrites of differing orientation. The colors represent composition variations in the system, while orientation differences are evident from the axes of the dendrite trunks.**

**Contributors and Collaborators:** G. B. McFadden and W. F. Mitchell (NIST/ITL) and R. Kobayashi (Hokkaido University, Japan)

# Processing-Structure-Property Data for Thermal Spray Coatings

*Reproducibility and reliability of thermal spray (TS) coatings are the major impediments to the realization of the full benefits of this technology. In addition, the processing procedures and properties of TS coating systems are not well documented or available. These needs have been addressed by the development and calibration of advanced sensors, applying these measurement tools to the control and characterization of TS coatings, and working with the TS community to establish a coating processing-microstructure-property database.*

Stephen D. Ridder

The focus of this project in FY2001 was on improving the reproducibility and reliability of thermal spray (TS) coatings through (1) evaluating the errors associated with improper use of non-contact thermometry (described above in the Highlights section), (2) characterizing the instabilities in the thermal spray deposition system, and (3) developing with leaders in the industry a coatings processing-microstructure-properties database. Participants at the NIST Thermal Spray Process Reliability workshop held in January, 2001 confirmed the importance of each of these research areas for NIST. Participants represented most major thermal spray processing equipment manufacturers, thermal spray users, national laboratories, and universities.

Significant progress was made in measurement of instabilities in the powder delivery and arc power systems in the thermal spray deposition system. A Coriolis meter in the powder delivery line was installed to measure powder mass flow-rate fluctuations has revealed the dynamics of powder flow. The most common technology for powder mass flow-rate control relies on the use of an electronic mass balance. As a result of the time constants inherent in the mass balance and in removing equipment vibration either by mechanical damping or by using electronic or software filters, the powder mass flow sampling rate is limited to approximately 0.1 Hz with the corresponding resolution of flow-rate fluctuations limited to <0.05 Hz. In contrast the Coriolis meter has a sampling rate >20 Hz, and therefore, can resolve flow-rate fluctuations >5 Hz. The improvement in resolution can be seen in the figure comparing the two flow-rate measurement techniques and the intensity from a photodiode, corresponding to an integrated light intensity from the plume. The impact of this fluctuation is that the time scale in the figure is proportional to a distance tranversed by the spray gun. This translates into a gradient in particle deposition rate and in particle velocities and temperatures, and, therefore, in coating thickness, microstructure, and properties.

A thermodynamic model of the plasma was developed that calculates the heat and momentum transfer to particles using thermodynamic and transport data for plasmas currently available in the literature. This model can be used to maintain particle velocities and temperatures in spite of changing gun conditions, including electrode wear, a major source of variability. The gun is typically controlled by specifying average arc current. As the electrodes wear, the physics of the arc changes and the power delivered to the plasma jet drops even with constant average arc current. This simple model is now available through an article in the Journal of Thermal Spray Technology.

The remaining activity is the development of a processing-structure-properties database for thermal spray coatings under consideration by the Information Development and Delivery Committee of the ASM Thermal Spray Society. This activity was proposed to the Committee by Christopher Berndt of SUNY, Richard Knight of Drexel University, and Steve Ridder of NIST. The TS community will provide data to be critically evaluated by a review group before inclusion in the database. It is envisioned that this database would be disseminated through equipment manufacturers as new thermal spray processing equipment is sold, through ASM and NIST to current users, and through the well-attended ASM short courses on "Thermal Spray Technology" taught by Berndt and Knight. NIST's role in this activity would be primarily in organization and data evaulation.

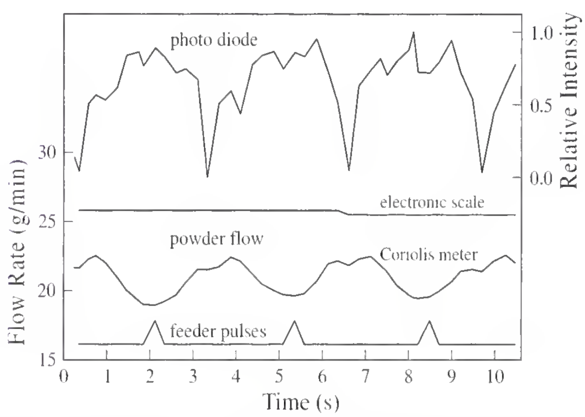



**Figure 1. Data from powder flow-rate sensors and photo diode showing improved temporal resolution and correlation of powder flow with powder feeder pulses .**

**Contributors and Collaborators:** F. S. Biancaniello, R. D. Jiggetts, S. P. Mates, and T. H. Gnäupel-Herold (NIST/MSEL) C. Presser (NIST/CSTL), J. F. Widmann (NIST/BFRL), D. Basak (University of Tennessee), and J. Geist (Sequoyah Technology LLC)

# Tailored Metallic Powders

*There is an intensive search for new "tailored" materials properties through manipulation of their microstructural components. The success of "creating" such materials is strongly dependent on how well we understand the relationships among properties, processing and microstructure. The objective of this research is to develop measurement techniques for the structural and chemical characterization of micro-engineered powders.*

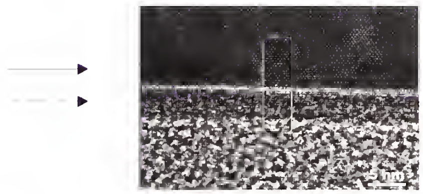
John Henry J. Scott (NIST/CSTL) and
Leonid A. Bendersky

The objective of this research is to develop measurement techniques for the structural and chemical characterization of microengineered powders – powders that are either intrinsically nanoscale or combine nanoscale coatings/layers with conventional micropowders. The availability of such measurement techniques will lead to improved understanding of critical microengineered powder fabrication processes such as chemical vapor deposition, physical vapor deposition, multilayer formation, powder agglomeration and sintering, interfacial reactions, and grain growth.

This year we concentrated on the following tasks: (1) Continue to improve the electron energy-loss spectroscopy (EELS) and energy-dispersive x-ray spectrometry (EDS) spectrum imaging methods, (2) Develop special TEM specimen preparation methods to study an interface between a base and a coating layer of nanoengineered powders, (3) Evaluate the capabilities and limitations of a recently acquired double-tilt/rotate TEM holder for manipulation of nanoparticles, and (4) Investigate new approaches to attain improved electron backscatter diffraction (EBSD) analysis of nanoscale particles.

In the first task, a new method for EELS spectrum-line imaging was developed. The imaging energy filter (EELS spectrometer) attached to a CM300FEG TEM was modified by insertion of a slotted grid in the entrance aperture. The electron optics in the filter are operated in a nonstandard mode to obtain a spectrum-line image, a profile data set containing one spatial dimension and one energy-loss spectrum simultaneously. Spectrum-line images were collected from ultrathin dielectric gate oxide film samples, demonstrating EELS profiling across nanometer-scale structures of technological importance (Figure 1).

In the fourth task, to improve the EBSD pattern quality for submicrometer particles, a sample holder was constructed that enables particle mounting on a thin, electron transparent substrate. The hypothesis was that the thin substrate would dramatically reduce the noise contribution from electrons that scatter into the substrate, and thus, improve pattern quality from small particles.



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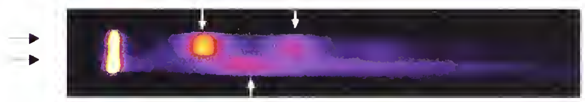

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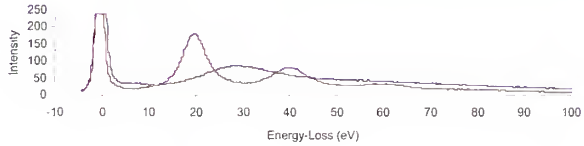


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**Figure 1. (a) TEM image of 5 nm $SiO_2$ gate dielectric film (bottom arrow) on a Si substrate (top arrow). (b) Spectrum line image of approximate area in yellow box in (a). Horizontal axis is energy loss in eV; vertical axis is position on sample in nm. White arrows indicate plasmon peaks. (c) EELS profiles from the spectrum line image.**

The hypothesis proved correct. The quality of the EBSD pattern from a 150 nm $Al_2O_3$ particle mounted on a 20 nm carbon thin-film is clearly superior to the pattern from the particle mounted on the bulk substrate. The pattern has a high enough signal-to-noise ratio to conduct a phase identification analysis of the particle and identify it as hexagonal $Al_2O_3$.

**Contributors and Collaborators:** S. Turner, J. H. J. Scott, and J. A. Small (NIST/CSTL)

# Electrochemical Processing of Nanostructural Materials

*The precise temporal control of supersaturation provided by electrochemical methods holds promise for the synthesis and characterization of materials and structures of very small dimensions – nanomaterials. Surfactants and segregation phenomena are investigated here for their role in controlling homo- and hetero-epitaxial film growth at the nanometer level. Measurements using proximal probes for directed synthesis are also being explored. Electrodeposition is also being used to produce materials of interest to the GMR and Spintronics projects in the MSEL Program on Materials for Magnetic Data Storage.*

Thomas P. Moffat

Metal-on-metal homo-epitaxial growth and hetero-epitaxial growth are topics of long standing scientific and technological interest. Remarkable progress has occurred in the last thirty years due to the application of ever more sophisticated analytical tools. In particular, the advent of a range of *in situ* methods has resulted in a renaissance in the study and application of electrochemical processing. Proximal probe methods are playing a central role in this development.

At NIST we are using Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) to examine the influence of inorganic surfactants such as halides and Group IIIa-IVa metals on the surface structure and electrodeposition of transition metals. These nominally simple systems exhibit quite complex behavior. For example, in the case of saturated halide adsorption, ordered 2-D adlayer structures are observed at potentials corresponding to the copper/cupric ion potential. In the presence of a metal deposition flux the adlayer floats on the surface and acts as a template which guides step motion. At more negative potentials a series of adlayer phase transitions occurs coincident with the decreasing coverage of halide. We are examining the influence of these surface phases on the metal deposition reaction as well as the possibility of using potential modulation to perturb the adlayer structure and thereby influence roughness evolution during metal deposition. Preliminary studies reveal a strong effect of potential modulation on roughness evolution during copper deposition in the presence of halide. This represents a first step towards understanding the influence of potential perturbation on electrocrystallization; a topic of some importance to the widely applied practice of pulse plating. In a similar manner underpotential deposition (upd) of metals is being explored for use as surfactants in homoepitaxial deposition or alternatively, as a novel processing scheme for producing alloys. Thus far, our work has centered on examining Pb upd on Cu. Clear evidence of a coverage dependent two-dimensional alloy-dealloying phase transition has been observed by voltammetric and STM studies of Cu(111), Cu(110) and Cu(100) and is a subject of ongoing study (Figure 1). Similarly, surface segregation of Cu during Cu/Co multilayer deposition on Cu(100) is also being examined.

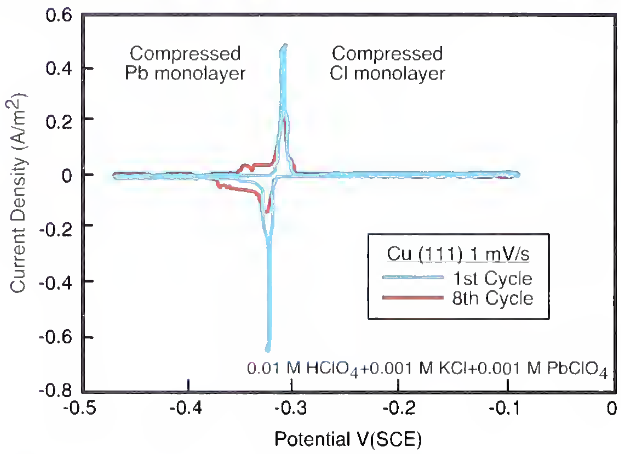


**Figure 1. Cyclic voltammetry reveals a potential driven 2-D phase transition between a halide and lead-covered Cu(111) surface. The peak current decreases and an additional peak appears with continued cycling of the potential. This reflects Pb alloying which accompanies the adsorbate driven step faceting.**

Metal-semiconductor contacts have been widely studied for interconnect applications. More recently, the realization of spin dependent transport effects has created a range of new opportunities from spin valves to metal-semiconductor spintronic devices. In the latter case, ferromagnetic metals may be used as a source of spin polarized electrons while semiconductors such as GaAs allow coherent transport of polarized electrons over a long range, up to 100 mm, suggesting all sorts of device possibilities. The literature suggests that the most difficult challenge is to transfer the polarized electrons from the ferromagnetic source into the non-ferromagnetic semiconductor without substantially degrading the polarization. Currently, the electrodeposition of bcc-Co on GaAs(100) is being studied. The good lattice match (<1 % misfit), is thought to stabilize a bcc-Co phase, which does not exist as a bulk phase. TEM provides evidence of the formation of 6 to 8 monolayers of this phase at the GaAs/Co interface which is subsequently covered by textured hcp Co. The possibility of stabilizing the bcc phase by adding Fe to the system is being explored.

**Contributors and Collaborators:** J. E. Bonevich, R. D. McMichael, M. Vaudin, D. E. Kramer, and T. Foecke (NIST/MSEL), A. Ford (NIST/SURF), W. Schwarzacher, (University of Bristol), and D. van Heerden (Johns Hopkins University)

# Reaction Path Analysis in Multicomponent Systems

*Many commercially important processes rely on multicomponent diffusion to control the formation and dissolution of precipitate phases with a matrix or at an interface. A multicomponent diffusion database for Ni-based superalloys developed at NIST provides a tool which enables modeling of various processes, including non-isothermal γ′ precipitation, heat treatment optimization, solidification, transient liquid phase bonding, and thermal barrier applications.*

Carelyn E. Campbell and William J. Boettinger

Multicomponent diffusion is important in many industrial processes, especially in the processing and application of Ni-based superalloys where diffusion determines the γ′ precipitate size and particle size distribution after solidification and heat treatment. An *a priori* understanding of this diffusion-controlled microstructure would allow the optimization of heat treatments that avoid incipient melting and the prediction of freezing temperatures and solidification paths for Ni-based superalloys. All of these processes require the use of a diffusion mobility database to describe the composition-dependent diffusion coefficients.

***Diffusion Mobility Database.*** Concentration-dependent diffusion coefficients in a multicomponent system are defined as the product of a thermodynamic factor and a mobility term. The NIST composition-dependent mobility database is being constructed using an approach which assumes that quaternary and higher order interactions are negligible. Thus, binary and ternary effects can be combined to extrapolate to higher order systems. For the Ni-Al-Cr-Co-Mo-Hf-Mo-Nb-Re-Ta-Ti-W system, a diffusion mobility database has been constructed for the γ (disordered FCC) phase. The current database includes only binary interactions. The database was validated using comparisons of the correlation of the melting temperature of the pure material with diffusivity, experimental quaternary diffusion coefficients, and other diffusion assessments. Diffusion calculations made with other thermodynamic databases have also been compared. The development of this diffusion mobility database has been submitted for publication and made available to industry.

Future work will incorporate diffusion in the ordered γ′ phase and development of a user-friendly electronic interface for public use. In addition, we are working with General Electric Corporate Research and Development (GE-CRD) and Howmet Corporation who will perform supporting experimental work. The experimental results will be analyzed by NIST and incorporated into the diffusion mobility assessments.

***γ′ Precipitation.*** The precipitation of the ordered phase, γ′, in the disordered γ (FCC) matrix is the dominant strengthening mechanism in Ni-based superalloys. Thus, control of the particle size distribution of γ′ is critical to achieving needed mechanical properties. As a part of a General Electric-led DARPA project, the γ′ precipitation process is being numerically modeled by Questek Innovations. This model requires inputs of equilibrium chemical potentials in γ and γ′, the composition dependent diffusivity in the γ matrix, γ and γ′ lattice parameters, and interfacial energy. NIST has provided Questek with an electronic version of the diffusion database to calculate the necessary diffusion coefficients.

***Homogenization.*** NIST has initiated an effort to develop heat treatment optimization techniques to address industry's need for more efficient heat-treating practices of cast Ni-based superalloys. The ideal heat treatment of a cast Ni-base superalloy consists of a heating schedule that avoids incipient melting while minimizing either the power expenditure or the heating time to achieve a homogeneous single phase structure. Initial simulations with linear heating rates have been completed for a Ni-Al-Ta alloy that had a liquid to γ to γ+γ′ solidification path. This model case demonstrated the potential for optimization. Future work will include investigation into the effects of non-linear heating rates and more rigorous optimization methods.

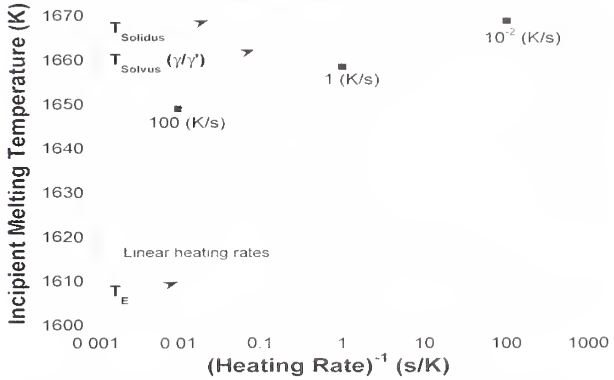


**Figure 1. Calculated incipient melting temperature as a function of linear heating rates for Ni-0.045Ta-0.12Al mole fraction alloy solidified assuming a Scheil solidification. Local equilibrium distributions of γ′ and $Ni_3Ta$ are assumed.**

**Contributors and Collaborators:** G. B. McFadden (NIST/ITL), R. F. Sekerka (Carnegie Mellon University), R. Reed (University of Cambridge), B. Muller (Howmet Corp.), J.-C. Zhao, (GE-CRD), and C. Kuehmann and H. Jou (Questek Innovations)

# Combinatorial Methods

The Combinatorial Methods Program develops new measurement techniques and experimental strategies needed for rapid acquisition and analysis of physical and chemical data of materials by industrial and research communities. A multidisciplinary team from the NIST Laboratories participates to address key mission-driven objectives in this new field, including needed measurement infrastructure, expanded capability, standards and evaluated data.

Measurement tools and techniques are developed to prepare and characterize materials over a controlled range of physical and chemical properties on a miniaturized scale with a high degree of automation and parallelization. Combinatorial approaches are used to validate measurement methods and predictive models when applied to small sample sizes. All aspects of the combinatorial process, from sample "library" design and library preparation to high-throughput assay and analysis, are integrated through the combinatorial informatics cycle for iterative refinement of measurements. The applicability of combinatorial methods to new materials and research problems is demonstrated to provide scientific credibility for this new R&D paradigm. One anticipated measure of the success of the program would be more efficient output of traditional NIST products of standard reference materials and evaluated data.

Through a set of cross-NIST collaborations in current research areas, we are working to establish the infrastructure that will serve as a basis for a broader effort in combinatorial research. A Combinatorial Methods Working Group (CMWG) actively discusses technical progress within NIST on combinatorial methods through regular meetings. The technical areas and activities of the CMWG are available in a brochure "Combinatorial Methods at NIST" (NISTIR 6730). Within MSEL, novel methods for combinatorial library preparation of polymer coatings have been designed to encompass variations of diverse physical and chemical properties, such as composition, coating thickness, processing temperature, surface texture and patterning. Vast amounts of data are generated in a few hours that promote our understanding of how these variables affect material properties, such as coatings wettability or phase miscibility. Additional focus areas for both organic and inorganic materials include multiphase materials, electronic materials, magnetic materials, biomaterials assay, and materials structure and properties characterization. State of the art on-line data analysis tools, process control methodology, and data archival methods are being developed as part of the program.

In order to promote communication and technology transfer with a wide range of industrial partners, an industry-national laboratories-university combinatorial consortium, the NIST Combinatorial Methods Center (NCMC), is being organized by MSEL. The NCMC will facilitate direct interactions on combinatorial measurement problems of broad industrial interest and efficient transfer of the methods developed to U.S. industry.

**Contact Information: Leonid A. Benderksy**

# Combinatorial Methods for Thin Films

*In the search for new functional materials for use in modern communication technology, a variety of complex oxides with different chemistry and structural states are under consideration. With the ability to measure locally the relevant dielectric and magnetic properties, combinatorial methods can have significant impact. The method can be used to create the "libraries" designed to either search a composition with an optimal set of physical properties or study fundamentals of the relationship between crystallo-chemistry and physical properties, e.g., polarization or magnetic ordering in complex oxides.*

Leonid A. Bendersky

Recently, the effectiveness of the combinatorial approach to the development of thin film electronic materials has been demonstrated. In this approach, in order to rapidly survey a large compositional landscape, combinatorial assays with up to thousands of compositionally varying cells are synthesized, processed, and screened in a single experiment. Dielectric and magnetic properties of the cells or compositional spreads can then be measured by using the recently developed scanning tip microwave near-field microscope (MNFM) and micro-superconducting quantum interference device (microSQUID), respectively. The properties, however, depend strongly on the microstructure of the thin films. In order to study the effect of library fabrication method on the observed structure-property relationships, combinatorial assays of thin films were prepared by two methods using controlled pulsed laser deposition: (1) deposition of cells using precursor layers, followed by post-deposition annealing, or (2) deposition of continuous compositional spreads using multiple targets controlled by synchronized shutters. Because the first method is quite versatile and requires relatively simple equipment, yet is unconventional as a production technique, it is of great interest to investigate the microstructural details of these films. It is also of great importance to understand and quantify the interdiffusion reaction in order to apply this combinatorial methodology to other materials.

In FY2001 we have continued our collaboration with the University of Maryland (Prof. I. Takeuchi) to investigate, using transmission electron microscopy (TEM), microstructural evolution in a model system of $BaTiO_3$ thin films fabricated from amorphous precursor multilayers consisting of $TiO_2$ and $BaF_2$. We have shown by TEM that with carefully controlled thermal treatments, the precursor $TiO_2$, $BaF_2/BaCO_3$, and $SrF_2/SrCO_3$ multilayers can be turned into predominantly single-phase epitaxial $(Ba,Sr)TiO_3$ films on lattice-matched substrates. We are also investigating the microstructure of $(Ba,Sr)TiO_3$ compositional spreads and have correlated the structural details (type and distribution of dislocations, defects) with measured dielectric properties.

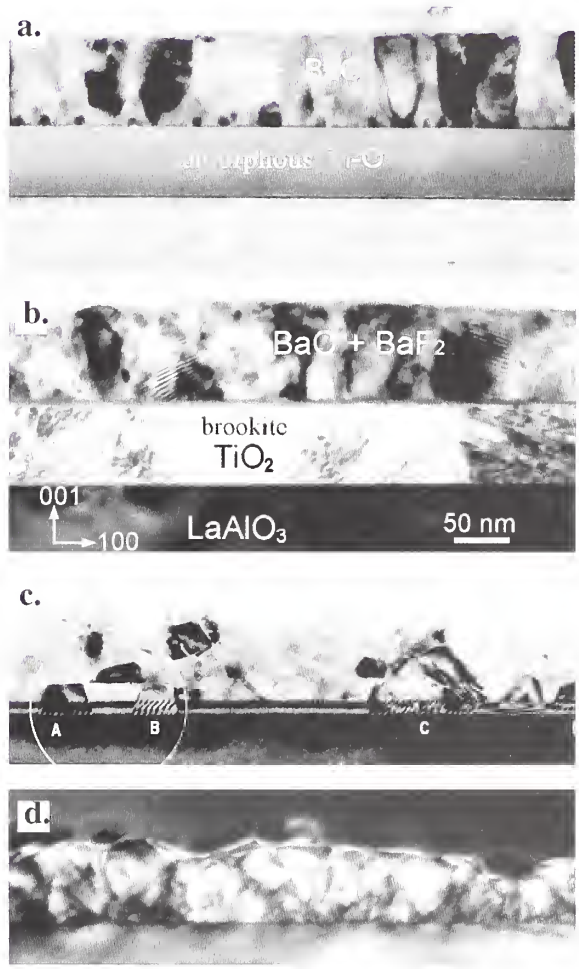


**Figure 1. A series of TEM micrographs showing the evolution of mixing of the $BaF_2$ and $TiO_2$ precursor layers. Microstructures at different stages of annealing of the precursors, (a) 200 °C; (b) 400 °C; (c) 700 °C and (d) 900 °C, are shown. From the investigation we concluded that epitaxial $BaTiO_3$ thin films of good quality can be formed by a nucleation and growth process on a substrate.**

**Contributors and Collaborators:** C. J. Lu, R. Parke, and M. Turchinskaya (NIST/MSEL), I.Takeuchi (University of Maryland), and X. D. Xiang (Lawrence Berkeley National Laboratory)

# Application of Phase Diagrams to Combinatorial Research: Interconnects to GaN Semiconductors

Albert V. Davydov, William J. Boettinger, and Ursula R. Kattner

*Gallium nitride based semiconductors find increasing application in photonic (blue LEDs, lasers) and microelectronic (high-power transistors) devices. Effective use of these devices requires improved electrical contact characteristics: lower resistance and higher thermal stability of metal contacts especially to p-GaN and AlGaN alloys. This project examines the properties of metal/GaN contacts and focuses on quantifying the relationship between the resistance of metal contacts and fundamental compositional, microstructural, and electronic properties of the metal/GaN interface. An improved understanding of these relationships will aid in designing optimal electrical contacts to GaN devices and demonstrate the utility of combinatorial methods in thin film research.*

Much industrial research currently focuses on Ti/Al-based metal contacts to n-GaN, aiming at the minimization of contact resistivity as a function of: a) semiconductor doping levels, b) metallization scheme (Ti/Al layer sequence and thickness, and alloy composition); and c) annealing treatment. We have employed thermodynamic and diffusion modeling of the Ti-Al-Ga-N system in combination with high-throughput (combinatorial) experiments to provide understanding for development of these contacts.

The combinatorial experiments involve the physical vapor deposition of Ti and Al on doped GaN in a patterned array of elements with different compositions. Each element will be subpatterned with a grid to enable the measurement of contact resistance. After annealing, those elements showing promising properties will be analyzed by cross-sectional scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Properties will be correlated to reaction products. An example of the subpattern grid for co-deposited Ti-Al metallization on GaN is shown in Figure 1.

To establish the thermodynamic basis for the combinatorial study, we have examined phase relations in two subsystems of the above quaternary system: Ti-Ga and Ti-Ga-N, where limited and contradictory data exist in the literature. Ti/Ga and Ti/GaN diffusion couples were characterized by x-ray diffraction and SEM/ x-ray energy dispersive spectroscopy. Interfacial phases were identified and compared with powder-sintered Ti-Ga and Ti-Ga-N alloys. The Ti/Ga couple (Fig. 2) unambiguously shows the following intermetallic phases in the Ti-Ga system: Ti(Ga) solid solutions, $Ti_3Ga$, $Ti_2Ga$, $Ti_5Ga_4$, TiGa, $Ti_2Ga_3$, $TiGa_2$, and $TiGa_3$. The homogeneity ranges of these compounds were also accurately determined at 1173 K. In the Ti/GaN diffusion couple, two new phases were identified: $Ti_3GaN$ (this phase was also found in the powder-sintered alloys) and a phase with a estimated composition of $Ti_3Ga_2N_2$.

The next step in this study is to reconcile the Ti/GaN diffusion path with the experimentally determined Ti-Ga-N phase diagram, so that predictions of diffusion reactions in more complex Ti-Al-Ga-N quaternary system can be estimated to help design the Ti/Al combinatorial metallization experiments.

As a first step in thermodynamic modeling, we are re-evaluating the Ga-N phase diagram including pressure influence on phase equilibria.

The results of this research were presented at the 30th International CALPHAD Conference (May 2001, York, UK) and 4th International Conference on Nitrides (July 2001, Denver, Co).

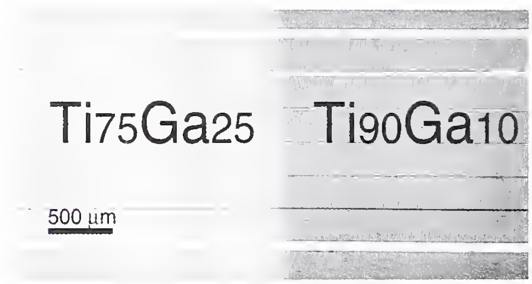


**Figure 1. Fragment of photolithographically patterned Ti-Al co-deposited metallization array (plane view): horizontal metal pads (gray, 75 % Ti and dark gray, 90 % Ti) are separated by gaps of various widths (white lines) for measuring contact resistance by transmission line method (TLM).**

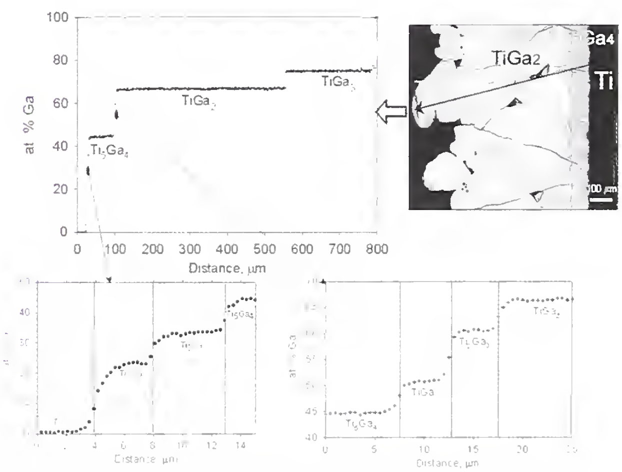


**Figure 2. Concentration profiles in the Ti/Ga diffusion couple after annealing at 800 °C for 430 hrs.**

**Contributors and Collaborators:** D. Josell, A. J. Shapiro, S. W. Claggett, and L. H. Robins (NIST/ MSEL), A.V. Davydov (University of Maryland), and V. Dmitriev (TDI)

# Data Evaluation and Delivery

Materials data are critical to the rapid and decentralized design and manufacture of communication, transportation and other devices, which characterize 21st century life. The goal of the Data Evaluation and Delivery Program is to provide the producers and users of materials with the means of fulfilling their data requirements in the most efficient ways. This goal is accomplished by providing improved access to materials data, developing methods for transferring materials data across the World Wide Web, providing protocols for data evaluation, and enhancing the functionality of existing collections of evaluated data. Much of this research is based on information technology and includes: the development of a materials mark-up language (MatML), the linkage of digitized crystallographic information with full structure analysis in cooperation with the International Center for Diffraction Data and Fachinformationszentrum (FIZ) Germany, and the production of phase diagrams through the NIST/American Ceramics Society Phase Equilibria Program. Other informatics available to the community are contained in the Ceramics WebBook at the Ceramics Division Website. The Ceramics WebBook provides links to other sources of ceramic data and manufacturer's information, selected evaluated data sets, structural ceramics and high temperature superconductor databases, glossaries, and tools for analysis of ceramic materials.

Databases for metals will be developed on web pages in the form of phase diagrams, deformation mechanism maps, and simple - but useful - interactive calculations of thermodynamic and mechanical properties. Annotation and interpretation will be conducted by the Metallurgy Division.

**Contact Information: Ursula R. Kattner**

# Thermodynamic Databases for Industrial Processes

*Many industries that process and use metals, from microelectronics to aerospace, need data for complex alloys (three or more components), including thermodynamic data describing behavior of alloys. The number of images that would be needed for graphical representation of these data is prohibitively large. Thus the development of thermodynamic databases that permit extrapolation of binary and ternary systems to higher order systems is needed. Access to these databases through an internet site with interactive software tools will allow the user to retrieve the needed phase diagram information.*

Ursula R. Kattner

In order to deliver materials data efficiently to the end user it is important to present technical data in a concise but useful form and utilize the interactive medium that the worldwide web offers for their retrieval. Downloaded databases and software for thermodynamic calculations are efficient for regular, expert users but are cumbersome for the occasional, less expert user. Retrieval of data through direct interaction with software on the server may be convenient for the occasional user, but may slow server responses significantly. The challenge is to develop interactive software for the potentially large set of non-expert users with sufficient versatility to allow complicated technical questions to be answered, sufficient speed to make the calculations efficient, and sufficient interpretation to allow the user to properly use the information.

In this project we will initially develop phase equilibria data on the web pages in the form of phase diagrams and simple, but useful, interactive calculations of thermodynamic properties, with sufficient annotation and interpretation to make them useful for the non-expert. In addition, the data on which these graphs are based will be available in the form of downloadable databases which can be processed into customized output by user software, or by specialized software developed by us and downloadable from our web site.

The phase diagram web site will also provide links to the NIST mechanical properties internet site allowing the user to examine the mechanical properties data that are available for the material.

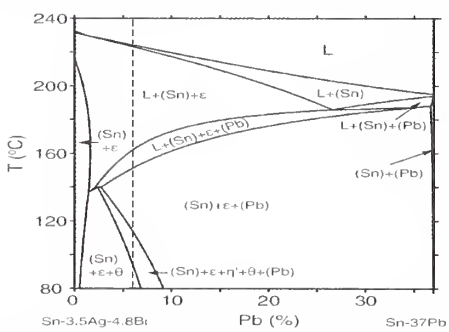


**Figure 1. Phase diagram for a Sn-3.5Ag-4.8Bi solder with contamination from a Sn-37 Pb solder.**

The following information has been posted on the site http://www.metallurgy.nist.gov/phase/

- An introductory page with links to information on phase diagram activities within the division and external links.
- A series of pages with ternary solder phase diagrams. Each page contains a calculated liquidus projection for Sn-rich systems and an enlargement of the Sn-rich corner and a table of the invariant reactions in the systems. The ternary systems currently available are: Ag-Bi-Cu, Ag-Bi-Pb, Ag-Bi-Sn, Ag-Cu-Pb, Ag-Cu-Sn, Ag-Pb-Sn, Bi-Cu-Pb, Bi-Cu-Sn and Cu-Pb-Sn.
- A link to files with the thermodynamic database description that was used to generate these phase diagrams.
- A tutorial page that illustrates the usage of phase diagram information for the case of Pb-contamination of Pb-free solder alloys. This page will also serve as an introduction to task-specific phase diagram software for the calculation of liquidus temperature, lever rule equilibrium and Scheil solidification.

Future work will include the development of easy-to-use interfaces for the task-specific software that will be posted either for interactive use or downloads on the on the web site. A *Best Practice Guide* for interpretation of differential thermal analysis (DTA) experiments will be integrated into the web site.

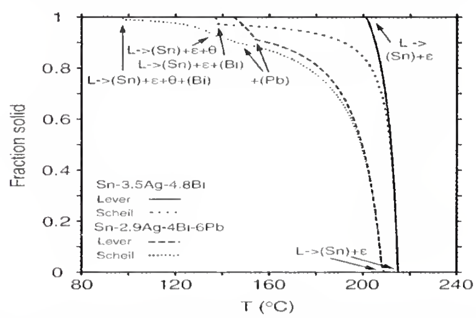


**Figure 2. Path for equilibrium and Scheil solidification of Sn-3.5Ag-4.8Bi with and without a 6 % Pb contamination.**

**Contributors and Collaborators:** W. J. Boettinger, R. J. Fields, and J. E. Bonevich (NIST/MSEL), and K.-W. Moon (University of Maryland)

# Mechanical Properties of Metals and Alloys on the Internet

*Mechanical properties are widely needed by U.S. industry for both estimates of materials performance and for use in finite element software. Critically evaluated data for many metal systems either do not exist or are hard to obtain by traditional literature search methods. This project's goals are to (1) develop a web site where users can easily find data generated or evaluated by NIST and (2) develop an interactive site where users can access the precise information they need from fracture and deformation mechanism maps.*

Richard J. Fields

Mechanical properties are used to predict the performance of metallic components during and after fabrication. There is a great abundance of mechanical properties data, but access to this data by traditional literature searching is a laborious, time consuming, and costly process. With the advent of the Internet, more and more scientists and engineers representing the full range of U.S. industry, academia, and government agencies search for data electronically almost to the exclusion of print media. There are already some sites that provide this information to a limited extent. This project intends to provide a special site for NIST generated or evaluated data, and a easily adaptable interactive site that will address more precisely the user's needs.

In the past year, the following information has been posted on the site http://www.metallurgy.nist.gov/materials_performance/

- Mechanical and physical properties of copper-tin and nickel- tin intermetallics
- Tension and torsion properties of eutectic Pb-Sn solder
- Fracture mechanism maps of copper, iron, and three steels (Figure 1)
- Deformation mechanism maps for LiF and NaCl
- Transient deformation mechanism maps for mild steel
- Crack growth mechanism maps (Figure 2)

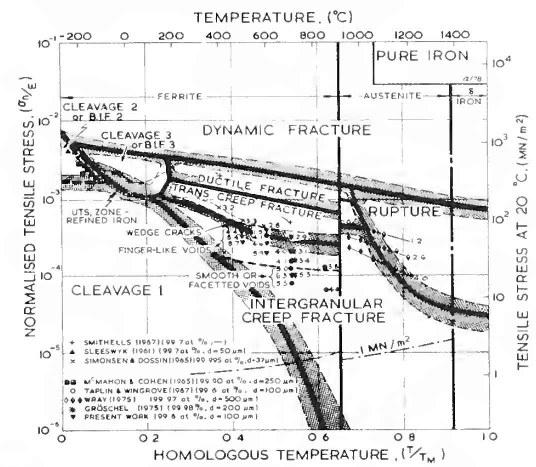


**Figure 1. Fracture Mechanism Map for Pure Iron**

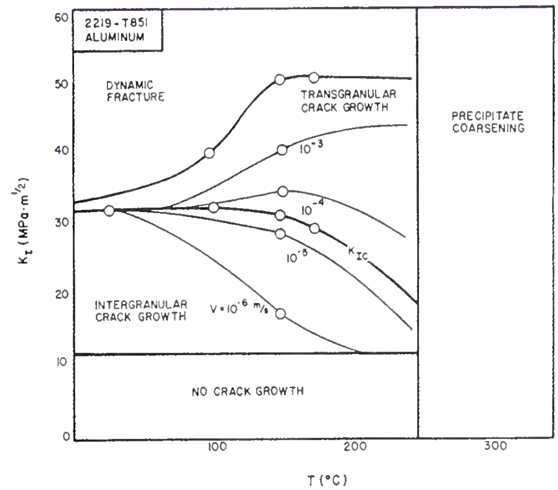


**Figure 2. A crack growth mechanism map for aluminum alloy 2219**

A useful feature of the NIST mechanical properties internet site is the ability to link to NIST phase diagram or thermochemistry data online by transferring to the phase information site for that material, and vice versa.

An effort was also begun in collaboration with Professor H. J. Frost of Dartmouth to have an online capability to access the high information density of deformation mechanism maps. These maps not only include most available data for a given material, but also provide constitutive equations that permit prediction of behavior in regions of stress and temperature of interest to the user, but where no data exists. This combination of deformation maps and constitutive equations will be a powerful tool for scientists and engineers to model and quantify the effects of microstructure, fabrication processes and use conditions on mechanical performance.

**Contributors and Collaborators:** U. R. Kattner and J. Bonevich (NIST/MSEL) and H. J. Frost (Dartmouth College)

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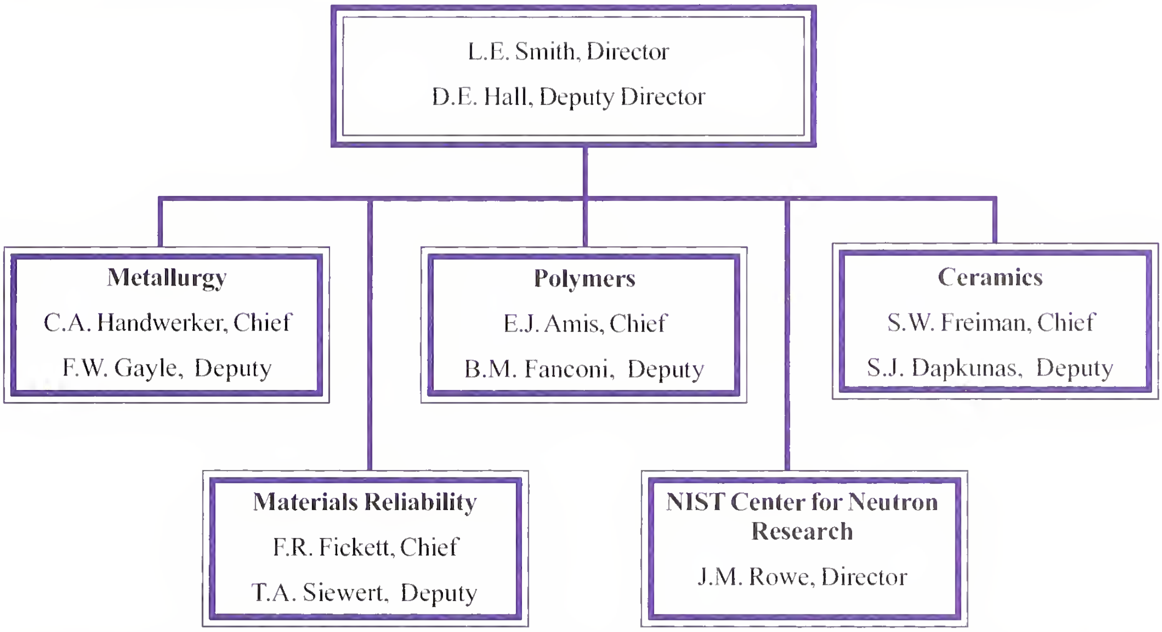


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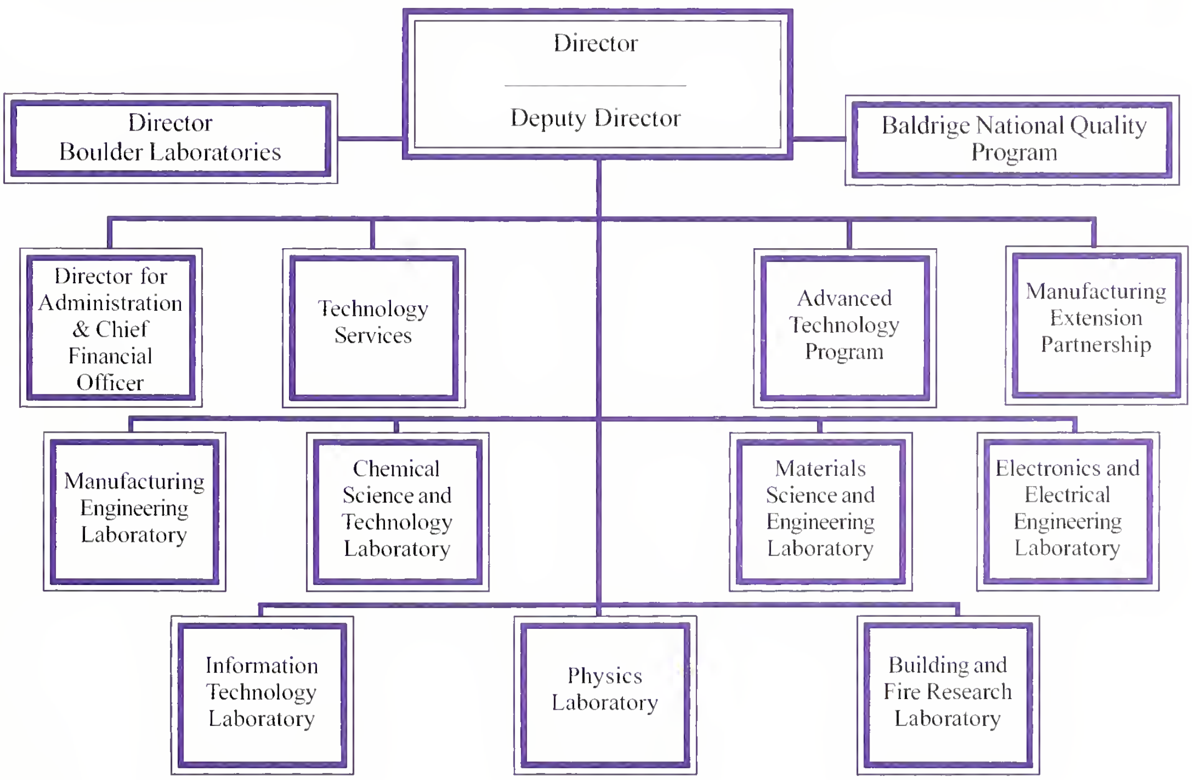

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